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1. INTRODUCTION AND SUMMARY

This annual summary report describes the work performed on the Integral Neutron Thermalization Program from October 1, 1966 through September 30, 1967, under Contract AT (04-3)-167, Project Agreement No. 2 with the U. S. Atomic Energy Commission. For a general review of the experimental, analytical, and theoretical investigations performed under this program, the reader is referred to the six previous annual summary reports. (Refs. 1 through 6).

During this contract year, considerable effort has gone into developing lattice dynamical models from first principles. The approach is expected to provide an improved physical understanding of the interactions of neutrons with bound moderator atoms. Up to now, beryllium (Section 6.2) and diamond (Appendix A) have been studied to exemplify the approach. The results have been encouraging, but much work remains to be done before the methods can be considered practical.

The code GASKET ⁽⁷⁾ was modified during this year to allow for diffusive modes of motion. Testing has begun. The inclusion of diffusive effects is part of our program to provide more accurate computation of the scattering laws for H₂O and other liquid hydrogenous moderators. The improved scattering law for H₂O will be used to further refine the multiple scattering corrections in H₂O samples. The model-sensitivity of these corrections has been studied intensively this year (Section 2.4). In addition, the improved scattering law for H₂O will be used to refine our calculation of neutron spectra in pure H₂O, which has never been satisfactory. ⁽⁸⁾

Benzene and molten diphenyl are also expected to benefit from the improvements to GASKET. ⁽⁷⁾ Benzene has been studied extensively this year, both

theoretically and experimentally with fairly good results. The experimental and theoretical research on this moderator are described in Sections 4 and Ref. 9 respectively, and have been combined for journal publication.⁽¹⁰⁾ The diphenyl spectrum measurements reported last year⁽⁶⁾ have been analyzed (Section 4.5) using the new scattering model for bound hydrogen in benzene. The results are unsatisfactory. These measurements will be reanalyzed with a scattering model for diphenyl that is now being developed (Section 4.4).

A central force model for zirconium hydride has been developed during this year. The model, which is described in Section 5.2, has been used successfully to calculate specific heats and to describe angular scattering measurements in that moderator (see also Section 5.3). The model will also be used soon to study some recently published⁽¹¹⁾ double differential scattering data for zirconium hydride. Refinements to this central force model may then be forthcoming.

Spectrum measurements have been made in beryllium metal at 77.4°K to check the adequacy of Young's⁽¹²⁾ scattering kernel for the moderator at that low temperature. It appears that the scattering kernel is adequate for many purposes despite the fact that it is computed in the incoherent approximation for this coherent scatterer. It is anticipated that coherent inelastic scattering by beryllium will be studied again this year for the purpose of preparing data suitable for ENDF.⁽¹³⁾ Speeding up the code COIN⁽¹⁴⁾ will be the expected approach. The spectrum measurements in beryllium oxide⁽⁶⁾ at elevated temperatures have not yet been analyzed. It is desired to use these observed data to test the scattering kernel for BeO based on Young's⁽¹⁵⁾ frequency spectrum. The development of this kernel is described in Section 6.4.

During this year, scattering laws for the bound light atoms in UO₂ and UC have been computed using a Debye frequency spectrum whose cutoff was adjusted to match the observed specific heats. Some numerical problems

were encountered, which are described in Section 7.2. These simple models may suffice until improved central force models become available. Such a model for UO_2 has been formulated and is described in Section 7.3. The recently published double differential scattering data on UO_2 and $\text{UC}^{(11)}$ will serve to test this and future models.

Various spectral studies in uranium have been performed this year. These include heterogeneous studies in the resolved resonance energy region that are described in Appendix B. These measurements were designed to demonstrate that techniques developed at General Atomic⁽¹⁶⁾ for studying position-dependent neutron spectra in thermal lattices could be applied at higher neutron energies and in media having strong resonances and large flux anisotropies. The results were found to be most promising. Spectrum measurements in a 20-inch diameter U^{238} sphere were made over the energy range 250 eV to 15 MeV at various positions and angles. These measurements were designed to check the cross section data for U^{238} and to check the calculational techniques which are commonly used in fast reactor design. The measurements have not been completely analyzed, but preliminary results are very promising. These results indicate that the spatial variation of the high energy flux near the source is probably a more critical test of the inelastic scattering cross sections than is the spatial change of the intermediate energy neutron spectrum. Time-dependent studies have been performed at various positions in the uranium sphere, which are described in Section 8.

Test spectrum measurements have been made in a near critical U^{235} sphere. These studies appear to show an overabundance of low energy neutrons in the spectra. Analysis of these data with improved geometrical representation is continuing. These two sets of measurements have demonstrated many of the capabilities at General Atomic for fast spectral studies. These measurements included the use of various flight paths up to 220 m in length, the on-line computer (CDC-1700), and a

series of detectors for each energy range. Much of this equipment has been furnished by the U. S. Atomic Energy Commission and will be used for further spectral measurements of importance to the fast breeder reactor program.

The experimental and theoretical data generated by this program have been disseminated by means of the General Atomic and EACRP Spectrum Books^(17, 18) and by submitting thermal scattering laws to the ENDF.⁽¹³⁾ The latter have been supplemented by a scattering law reference manual whose contents and objectives are described in Section 11. It is anticipated that the Spectrum Book⁽¹⁷⁾ will incorporate fast spectral data including those from the U^{235} and U^{238} sphere experiments. Other information has been disseminated by means of topical reports, journal articles and presentation at meetings (see Refs. 8, 9, 10, 26, 27, 29, 35, 46, 56, 112-127).

2. NEUTRON THERMALIZATION IN H_2O AND D_2O

2.1 INTRODUCTION

Studies of thermalization in H_2O and D_2O during the past year have been strongly influenced by the fact that a fundamental theoretical description of the liquid state is not presently available and is not expected in the near future. Hence, progress in understanding low energy neutron scattering by these important moderators depends on the accumulation of experimental data and the correlation of such data by semi-phenomenological models. Two models which are frequently discussed in the literature and which are typical of the most advanced theoretical water scattering laws yet developed are the Haywood II kernel,⁽¹⁹⁾ developed at General Atomic, and the McMurry-Russell model.⁽²⁰⁾ These models have recently been compared with double differential data taken at RPI.⁽²¹⁾ The comparisons show areas of good agreement as well as areas of substantial disagreement both between theories and data and between the theories themselves. These results show the need for improvement in the phenomenology. Some efforts in this direction have been accomplished by the inclusion of diffusive modes in the General Atomic scattering law code GASKET⁽⁷⁾ as described in Section 12.1 of this report.

While double differential measurements constitute a very severe test of theoretical models, their interpretation is greatly complicated by the necessity to correct for resolution effects and for multiple scattering. The multiple scattering corrections, in particular, introduce an inherent uncertainty which can lead to serious misinterpretation of the data. The results of additional studies of the effects of multiple scattering on water data are described in Section 2.4.

Integral data such as single differential and total cross sections and neutron spectra are obtainable with greater precision than double differential data and thus provide a test of theoretical models which, while less severe, is less ambiguous. Sections 2.2 and 2.3 describe such measurements for H_2O made in the past year at General Atomic, and show comparisons with theoretical calculations.

The situation for D_2O is complicated by the fact that, in contrast to H_2O , heavy water is essentially a coherent scatterer. Nevertheless because of a fortuitous cancellation, interference scattering can be neglected in total cross section calculations and in most transport calculations.⁽²²⁾ However, interference cannot be neglected in the calculation of single and double differential cross sections. The code GASKET⁽⁷⁾ was designed for use in the incoherent approximation and therefore cannot give precise results in D_2O scattering law calculations. Nevertheless, GASKET calculations have been used to generate data for ENDF. Haywood and Page⁽²³⁾ have in fact shown that a model based on a continuous frequency distribution can fit D_2O scattering law data in an average sense, even though the incoherent approximation is used.

While models for D_2O , which include interference do exist,^(22, 24) they are restricted to describing the so-called hindered rotations of the molecule by a single discrete frequency rather than by a more physical continuous distribution. Such a model, like the Nelkin model for H_2O ,⁽²⁵⁾ cannot be expected to give detailed fits to double differential data and consequently⁽²⁶⁾ cannot be used confidently in computing multiple scattering calculations. Thus, additional measurements for D_2O will be of limited value until improved theoretical models which include both interference and a continuous frequency distribution are available for interpreting the results.

2.2 SINGLE DIFFERENTIAL SCATTERING FROM LIGHT WATER

During the last few years the measurement of single differential neutron scattering from light water has been performed with the high intensity thermal neutron source developed by the General Atomic LINAC. The single differential cross sections have been measured over the energy range 0.006 eV to 10 eV. The experimental techniques for making the measurement and correcting the data to obtain an absolute cross section are discussed in a recent article⁽²⁷⁾ which has been submitted to Nuclear Science and Engineering. It has been found that the multiple scattering of neutrons in the samples constitutes a large effect, therefore procedures⁽²⁶⁾ were developed and tested in many configurations for making this correction. The resulting cross sections were compared with predictions of theoretical models describing the molecular motion in water. These models include various versions of the free gas model, the Nelkin model,⁽²⁵⁾ the Haywood II model,⁽¹⁹⁾ the McMurry model,⁽²⁰⁾ and the Radkowsky prescription.⁽²⁸⁾ Completely satisfactory agreement with all of the available neutron scattering data does not appear possible for any of the above models. The Haywood II model⁽¹⁹⁾ seems on the whole to provide the most nearly acceptable agreement over a wide range of data and in particular gives good agreement with single differential data. These experimental data will be incorporated into the ENDF⁽¹³⁾ in the near future so that they may be used in further testing efforts. Aside from the importance of these measurements as a sensitive check on the models for neutron scattering, these data are also very useful for comparison with results from double differential cross section experiments.

2.3 TOTAL CROSS SECTION OF H₂O

A measurement of the total cross section σ_T for H₂O was performed at General Atomic four years ago.⁽³⁾ It has become desirable to incorporate these data in the Evaluated Nuclear Data File, ENDF.⁽¹³⁾ The measurements were previously⁽³⁾ submitted to a preliminary analysis. During

this year a further analysis, which is described in detail in a topical report,⁽²⁹⁾ has been performed. In this analysis, we have corrected for previous errors which included: (1) a 0.2% error in the energy determination; (2) the neglect of data from one sample; (3) the neglect of uncertainties in the sample thickness; and, (4) the non-usage of weighting factors in averaging σ_T for comparison to theoretical values. In this section, we summarize the results which are detailed in Ref. 29. Figure 2.1 shows the resulting σ_T data for H_2O . They appear to be an improvement over that in the literature and agree fairly well with the low energy chopper data of Hughes.⁽³⁰⁾ Figure 2.2 compares the ratios of the total cross sections predicted by the various scattering models for H_2O to the observed values. No one model appears to be satisfactory. In general, the Koppel anisotropic model⁽³¹⁾ and the Haywood II model⁽¹⁹⁾ predict σ_T closer to the measured values than does the Nelkin model.⁽²⁵⁾ This conclusion is identical to that arrived at by Koppel⁽¹⁹⁾ and by Young.⁽³²⁾ There are too few data points to draw any conclusions on the relative accuracy of the McMurry-Russell model.⁽²⁰⁾ Some discrepancies remain between theory and measurement.

It has been possible to use the measured total cross sections to calculate $\bar{T}$, 2/3 of the average kinetic energy of the bound hydrogen atoms in H_2O . The value for $\bar{T}$ quoted in Ref. 29 may not be correct since the relation between σ_T and $\bar{T}$ was not treated properly. This part of the analysis is therefore being re-evaluated.

2.4 MULTIPLE SCATTERING IN DOUBLE DIFFERENTIAL MEASUREMENTS

It has become generally recognized that correction for multiple scattering is a highly important part of the data reduction process for double differential measurements.⁽²⁶⁾ Recent presentations of experimental data have laid considerable stress on the differences to be expected between corrected and uncorrected data.^(11, 23, 33, 34) However, in many cases the inherent uncertainty of the correction methods appears to be less widely

Fig. 2.1--Measured total cross section of H₂O

Fig. 2.2--Ratio of predicted to observed total cross section for H_2O

appreciated. Two basically different methods of multiple scattering correction - the factor method and the subtraction method - were described in Ref. 26 and applied to room temperature water data. It was found that the corrections were sensitive to both the correction method and to the theoretical model used in the computation of multi-collision fluxes. The choice of correction method, and the usefulness of the resulting corrections were found to depend on complicated and interrelated considerations involving both the theoretical model and the experiment.

In the past year the accuracy of correction methods has been more deeply investigated and further recommendations concerning the treatment of multiple scattering have been offered. Also, the calculation of corrections has been extended to zirconium hydride, to which a new lattice dynamical model has been applied (see Section 5.2). These results have been presented in a new topical report,⁽³⁵⁾ which also reviews the correction methods and presents results of a hypothetical "experiment" in which "corrected data" can be compared with a known answer.

Some consideration has also been given to the dependence of multiple scattering corrections on variables in the experimental setup, such as sample thickness and orientation. Correction factors for a water upscattering experiment (.0052 eV incident neutron energy) as a function of sample thickness have been computed and are shown in Ref. 35. It was found that such corrections are insensitive to the sample thickness over a wide range of thicknesses. This result suggests that the method of checking experimentally for multiple scattering by reducing sample thickness until experimental results are no longer affected is not a reliable test. In fact, this conclusion typifies what appears to be a general characteristic of experimental tests for multiple scattering: results of such tests can show the presence of multiple scattering but they cannot prove unambiguously that it is absent.

Thus, the need for detailed theoretical multiple scattering calculations like those described in Refs. 26 and 35 apparently cannot be avoided solely by introducing changes in experimental setups.

3. NEUTRON THERMALIZATION IN POLYETHYLENE

3.1 INTRODUCTION

Despite the considerable effort applied in the past to the study of neutron thermalization in polyethylene, significant discrepancies between theory and experiment remain to be explained. The most important one is the difference between the theoretical⁽³⁶⁾ effective temperature $\bar{T}$ and the value obtained from the measurement⁽³⁷⁾ of epithermal total scattering cross sections. The experimental $\bar{T}$ is about 30% higher than the predicted value. A discrepancy pointing in the same direction appears in the measurement of thermal neutron spectra.⁽³⁸⁾ In both instances, the agreement can be considerably improved by increasing the cutoff frequency of the vibrational spectrum used in the calculations. This, however, would contradict optical measurements, which definitely set the cutoff at about .36 eV. Hence, more study in this field is warranted.

Although in the past year no additional theoretical calculations have been done on polyethylene, some improvement has been achieved in the experimental techniques; this will be described in Section 3.2.

3.2 ANGULAR SCATTERING CROSS SECTION OF CH₂

The angular scattering cross section of polyethylene was measured for a set of incident energies and reported in the previous annual report.⁽⁶⁾ Since that time the technique of angular scattering measurements has undergone a number of improvements. These improvements, which were developed while making the measurements on $\text{ZrH}_{1.85}$ and C_6H_6 , and described in Sections 5.3 and 4.3, are the following:

1. The introduction of a new pair of monitors located on the direct beam, a fission chamber before the sample, and a BF_3 bank after the sample.
2. The use of graphic recorders to check continuously the response of the monitors. This has notably increased the reliability and accuracy of the monitor system.
3. A better way of calculating the correction due to the finite length of the flight path after scattering. The correction has been computed performing an integration over time to get the time-of-flight spectrum actually measured. The correction procedure is described in Section 12.4.

Because of these improvements in the technique we feel that the results on $\text{ZrH}_{1.85}$ and C_6H_6 are more accurate than the results previously reported on CH_2 . Therefore, a new set of measurements of the single differential cross section of polyethylene has been programmed and will be performed in the near future.

4. NEUTRON THERMALIZATION IN BENZENE AND DIPHENYL

4.1 INTRODUCTION

During this year considerable progress has been made in our understanding of neutron thermalization in benzene and diphenyl. A scattering model for benzene has been formulated and has been tested against Gläser's scattering law data,⁽³⁹⁾ against a neutron spectrum measurement,⁽⁴⁰⁾ and the angular scattering cross section measurements of Hofmeyer.⁽⁴¹⁾ In addition, new measurements have been made this year of the total cross section of benzene (described in Section 4.2) and of the angular scattering cross section (described in Section 4.3). These data have been compared to the predictions of the new scattering model and found to show a good agreement. Since the scattering model has been described in a topical report⁽⁹⁾ and has been discussed at the Ann Arbor Conference on Neutron Thermalization no further description is given in this section. A similar model formulated by McMurry⁽⁴²⁾ was also given at that conference. The theory and the comparison to measurement has also been written up for journal publication.⁽¹⁰⁾

Spectral measurements were made during this year in molten diphenyl (80°C) at various poison concentrations. Spectrum measurements were also made in the vicinity of a D₂O-diphenyl interface. These studies are described in Section 4.5. The measured data have been analyzed using the theoretical bound model for hydrogen in benzene to describe the scattering by hydrogen in diphenyl. The agreement is not satisfactory, and a further analysis will be undertaken soon using the more recently developed model for diphenyl, which is described in Section 4.4.

4.2 TOTAL CROSS SECTION OF BENZENE

The total cross section of benzene was measured during this year to provide data for comparison to the new scattering model due to Sprevak and Koppel.⁽⁹⁾ The measurement utilized the experimental arrangement illustrated in Fig. 4.1. This arrangement provided a clean geometry that was so well shielded that the background could be ignored. The neutrons were produced by pulsing the electron beam onto a water cooled fansteel target placed in front of a 1-1/2-inch thick slab of pure polyethylene. The target and moderator were in turn shielded by means of thick boron-loaded shields. The room return in this arrangement was found to be negligible. The detector used was a bank of four two-inch diameter BF_3 detectors, each having an active length of 15 cms.

Three sample thicknesses were used: 93 mils, 193 mils, and 313 mils. The pulsed neutron source intensity was maintained by means of gold foils, by two BF_3 detectors along the flight path, and by two room return monitors. Detector and monitor drifts were partially accounted for by interspersing the runs. Each sample transmission measurement was followed by a dummy sample transmission measurement. Each sample was measured twice. The data were reduced by means of the code HECTO,⁽⁴³⁾ which corrects for count rate losses and the mean emission time of neutrons from the source-moderator, and also subtracts the background and groups the channels to improve the counting statistics. HECTO finally computes the observed neutron spectrum and its statistical uncertainty. The spectra thus calculated were used to compute the total cross section and its uncertainty, making allowance for in-scattering and multiple scattering with the procedures of Ref. 29. The results from the six runs (two measurements for each of three sample thicknesses) were weighted and averaged.

The measured data are compared to the predictions of the Sprevak⁽⁹⁾ model in Fig. 4.2. The theoretical model predictions show

Fig. 4.1--Geometry for angular scattering and total cross section measurements

Fig. 4.2--Comparison of experimental and calculated total cross sections for benzene

a similar shape and magnitude to the observed values. Some structure predicted by the calculations around 0.15 eV is observed in the measured σ_T . The theoretical data are consistently lower than the measurements though not by a consistent amount or by a ratio factor that would permit speculation on the cause of the discrepancy. The discrepancy between theory and the measured data, however, is larger than the statistical uncertainties which are generally smaller than the dots themselves. On the whole, experiment and theory agree to better than 2.5% and thus provide support for the adequacy of the Sprevak model for benzene.

An attempt has been made to use the Placzek expansion,⁽⁴⁴⁾ given below, to compute $\bar{T}$ for hydrogen in benzene:

$$\sigma_T/6 \text{ (Benzene)} = \sigma_{s.C} + \sigma_{a.H}(E) + \sigma_{fa.H}(1 + \bar{T}/2ME)$$

$\bar{T}$ is 2/3 of the average kinetic energy of the bound hydrogen atom in benzene. This expansion can sometimes be used to obtain a measured $\bar{T}$ which can be compared to the theoretical value computed by GASKET.⁽⁷⁾ In this study the relatively thin sizes of the samples gave less precise values than when a similar study was performed with H_2O .⁽²⁹⁾ In the experiment we found $\sigma_{fa} = 20.35 \pm 0.15$ barns and $\bar{T} = 0.08922 \pm 0.01070$ eV. These compare to the accepted⁽³⁰⁾ free atom value for hydrogen of 20.36 barns and the computed $\bar{T}$ of 0.10046 eV for the Sprevak model. The theoretical $\bar{T}$ agrees with the measured value within the experimental errors. These errors are large enough, unfortunately, to cover significant model differences.

4.3 ANGULAR SCATTERING CROSS SECTION OF C_6H_6

The single differential cross section has been measured for benzene using a sample having an average thickness of 0.119 cm. The technique used for the collection and the analysis of the data was the same as that used for CH_2 , described in Ref. 6. The sample was contained in a sealed

holder consisting of an aluminum ring between two stretched aluminum foils each 5 mils thick. The sample thickness was carefully checked for possible bulging after filling. The maximum variation in sample thickness did not exceed 5%. The product $\Sigma_T d$, Σ_T being the total macroscopic scattering cross section, and d the thickness of the sample, was 0.362 for an energy of 0.01 eV, so that the transmission at this energy was about 70%. The maximum amount of multiple scattering as calculated by MUSE⁽⁴⁵⁾ did not exceed 45%.

Figure 4.3 shows the measured single differential cross section for benzene as a function of scattering angle at seven selected energies. The continuous curves in the figure are the result of a calculation using a kernel computed by Sprevak and Koppel.⁽⁹⁾ This kernel was evaluated with the code GASKET⁽⁷⁾ assuming a single oscillator for the cluster of frequencies near 0.38 eV and an artificially broadened frequency spectrum for the part below 0.38 eV. The scattering from the hydrogen atoms and from the carbon atoms in the benzene ring was included in the computation and treated in the incoherent approximation. The kernel was used to compute the corrections for multiple scattering and finite flight path.

As in the case of polyethylene⁽⁶⁾ the results are dependable in an angular range above 30 degrees. The geometrical constant which gives the absolute values of the cross section was determined by normalization to the experimental total cross section (see Section 4.2). The angular integration over the experimental results to obtain the normalization constant is only slightly influenced by the uncertainty in the correction factors below 30 degrees. Because of the presence of the factor $\sin \theta$ in the integrand that gives the total cross section, the low angle values do not affect the results too much. The values of the normalization constant including or not including the corrections for angles below 30 degrees differ at most by 3%. Due to an improved data collection procedure, the experimental errors in the benzene measurement are believed to be smaller than in the case of CH_2 .⁽⁴⁶⁾ The dimension of the experimental points in Fig. 4.3 corresponds to the statistical error.

Fig. 4.3--Angular scattering cross section of benzene

Some oscillations due to coherent effects, which cannot be accounted for by the model, are visible at low energies. The average cosine of the scattering angle $\bar{\mu}$ was computed and is shown in Fig. 4.4 together with the computed theoretical curve of Sprevak and Koppel.⁽⁹⁾ The agreement is good. Measurements of the single differential cross section of benzene have been reported by Hofmeyer⁽⁴¹⁾ at four incident energies, using a monochromatic beam obtained by crystal diffraction from a reactor beam. His procedure of correcting for multiple scattering used Vineyard's⁽⁴⁷⁾ approximation of isotropic multiple scattering and hence is less general than a MUSE calculation.⁽⁴⁵⁾ Figure 4.5 shows a comparison between the results of Hofmeyer and our results at comparable energies. The two sets of measurements agree well except at high scattering angle for an incident angle for an incident energy of 0.025 eV. The difference is believed to be due to the different way of treating the multiple scattering.

4.4 A MODEL FOR THE DESCRIPTION OF THE MOLECULAR DYNAMICS OF DIPHENYL (C₁₂-H₁₀)

In the equilibrium configuration and in the liquid and solid state the diphenyl molecule is planar and has a structure formed by two benzene rings joined at two carbon atoms, with the symmetry of the D_{2h} group. The description of this configuration is given in Fig. 4.6, where the small circles correspond to the hydrogen atoms and the big circles to the carbon atoms. The geometrical parameters were taken from the values obtained by Trotter.⁽⁴⁸⁾

For the description of the internal motions of the atoms forming the molecule it was found very convenient to use the valence coordinates defined by Wilson et al.⁽⁴⁹⁾ That is, for the coordinates describing the inplane motions:

R_{ij} = The carbon-carbon bond stretching

r_{ij} = The carbon-hydrogen bond stretching

Fig. 4.4--Average cosine of the scattering angle for benzene

Fig. 4.5--Angular scattering cross sections for benzene; comparison of two experimental results

Fig. 4.6--Geometry of the diphenyl molecule; the distances are given in angstroms and the angles in degrees

α_j = The change in the CCC ring angle

β_j = The angle between the CH bond and the bisector of the outer CCC angle. The definition for the diphenyl molecule of these coordinates is described in Fig. 4.7.

For the out-of-plane motions, the following set of valence coordinates was used:

between the C_iX_i bond ($X = H$, or the C in the adjacent ring) and the plane formed by the i -th carbon atom and its two adjacent carbon neighbors; $\Delta\tau_i =$, the change in angle between $C_{i-1}C_iC_{i+1}C_{i+2}$ plane. In Fig. 4.8 the coordinates describing the out-of-plane motions are specified.

Because diphenyl is a planar molecule, its normal vibrations are of two kinds. One set of normal vibrations has amplitude vectors that are perpendicular to the plane of the molecule and the other set has amplitude vectors that are parallel to the plane of the molecule. Altogether there are $3n-6 = 60$ normal modes of vibration. Of these, $2n-3 = 41$ are of the parallel type. The remaining 19 modes belong to the perpendicular type. Using the properties of symmetry corresponding to the group D_{2h} the secular equation corresponding to the vibrational problem can be factorized by a transformation of coordinates. Each factor of the secular equation corresponds to a particular class or symmetry species of the D_{2h} group. The factorized secular equation for the inplane motion is formed by four blocks, each of these corresponding to the following identification: 11 A_g , 10 B_{2u} , 10 B_{1g} , and 10 B_{3u} ; the first numbers in the identification of the symmetry species correspond to the dimension of the block associated with the particular symmetry. For the out-of-plane vibrations, the secular equation reduces to four blocks corresponding to the classes: 6 B_{1u} , 4 A_u , 3 B_{3g} , and 6 B_{2g} .

Fig. 4.7--Definition of the valence coordinates for the in-plane vibrations

Fig. 4.8--Definition of the valence coordinates for the out-of-plane vibrations

The force constants for a simplified valence force field (VFF) of diphenyl were obtained by refining the set of force constants used for benzene in previous work,⁽⁹⁾ by a least squares technique and using the assignment of Peregudov⁽⁵⁰⁾ for the harmonic frequencies. The definition of the force constants are described in Figs. 4.7 and 4.8 and their final values in Figs. 4.9 and 4.10. The calculated and observed frequencies are given in Tables 4.1 and 4.2.

With the refined set of force constants, the frequency spectrum was calculated and is shown in Fig. 4.11. The set of vibrational frequencies closely spaced about .38 eV in the spectrum of vibration of $C_{12}H_{10}$ will be considered as a single oscillator for the calculation of the neutron scattering kernel and are not shown in Fig. 4.11. This frequency spectrum will be used to compute the scattering law for $C_{12}H_{10}$.

4.5 THERMAL NEUTRON SPECTRA IN DIPHENYL AND AT A DIPHENYL- D_2O INTERFACE

Since the scattering model for diphenyl described in Section 4.4 was not available at the beginning of this year, Sprevak's scattering model⁽⁹⁾ for benzene was used to analyze the spectral measurements in diphenyl and at a diphenyl- D_2O interface that were performed and reported⁽⁶⁾ in the previous year. This approach seemed reasonable since benzene is the simplest of all the polyphenyls and a similarity in the bound motion of the hydrogen atoms was to be expected. In brief, the measurements which were analyzed comprised:

1. A series of quasi infinite-medium thermal spectrum measurements in a 10 in. by 10 in. by 10 in. tank of molten diphenyl at various poison (ethyl borate) concentrations.
2. Position-dependent spectrum measurements around the interface between a 12 in. by 8 in. by 4 in. tank of molten ($80^\circ C$) diphenyl adjacent to a 12 in. by 8 in. by 12 in. tank of D_2O at the same temperature. The diphenyl was poisoned by ethyl borate to 3.90 barns/H atom at 2200 m/sec and the D_2O was

Fig. 4.9--Definitions and least squares values for a 9 parameter VFF for the out-of-plane vibrations of diphenyl.
The force constants are in units of 10^{-11} erg/rad²

1		6.501	8		1.127
2		5.059	9		2.331
3		0.994	10		0.736
4		-0.652	11		0.232
5		-0.251	12		0.672
6		0.579	13		1.191
7		0.276	14		0.662
15		4.333			
16		-0.182			
17		-0.459			

Fig. 4.10--Definitions and least squares values for a 17-parameter VFF for the in-plane vibrations of diphenyl.

Stretch constants are in units of mdyn/rad; bending and torsion constants are in units of mdyn A⁰/rad²

Fig. 4.11--Frequency spectrum of hydrogen atoms in $C_{12}H_{10}$
(The set of frequencies about .38 eV are not shown)

Table 4.1

OBSERVED AND CALCULATED FREQUENCIES FOR THE
IN-PLANE MODES

<u>Observed Freq.</u> <u>cm-1</u>	<u>Calculated Freq.</u> <u>cm-1</u>	<u>Percent Error</u>
<u>Symmetry Class Alg</u>		
	3060.3	
3060	3056.0	0.130
3047	3051.1	0.134
1612	1644.8	2.035
1504	1488.6	1.023
1280	1344.9	5.071
1185	1124.4	5.111
1032	1024.2	0.755
1003	912.2	9.050
740	787.0	6.346
315	290.9	7.641
<u>Symmetry Class Blg</u>		
	3053.3	
3047	3052.4	0.177
1592	1668.0	4.775
1452	1523.1	4.894
1325	1429.5	7.886
	1142.3	
1155	1115.2	3.445
1092	1037.2	5.015
612	580.5	5.146
407	394.3	3.116
<u>Symmetry Class B2u</u>		
3096	3053.6	1.370
3047	3052.5	0.180
1580	1671.9	5.817
1440	1532.4	6.419
1326	1413.2	6.578
1280	1232.1	3.745
1170	1117.8	3.257
	590.7	
	108.7	
<u>Symmetry Class B3u</u>		
3069	3061.0	0.262
3047	3056.1	0.298

Table 4.1 (cont)

<u>Observed Freq.</u> <u>cm-1</u>	<u>Calculated Freq.</u> <u>cm-1</u>	<u>Percent Error</u>
<u>Symmetry Class B3u</u>		
3010	3051.1	1.367
1600	1584.6	0.965
1492	1458.6	2.241
1190	1196.6	0.553
1050	1090.9	3.895
1016	1912.0	0.389
996	906.1	9.029

Table 4.2

OBSERVED AND CALCULATED FREQUENCIES FOR THE
OUT-OF-PLANE MODES

<u>Observed Freq.</u> <u>cm-1</u>	<u>Calculated Freq.</u> <u>cm-1</u>	<u>Percent Error</u>
<u>Symmetry Class Blu</u>		
974	963.7	1.059
904	904.9	0.097
724	767.9	6.066
688	674.5	1.965
	439.6	
	35.9	
<u>Symmetry Class Au</u>		
	967.5	
	854.4	
	417.	
	119.6	
<u>Symmetry Class B3g</u>		
965	964.9	0.016
838	852.6	1.740
407	394.3	3.115
<u>Symmetry Class B2g</u>		
980	993.5	1.375
897	947.3	5.606
780	807.7	3.554
	702.8	
540	547.7	1.431
267	203.2	23.881

poisoned by cadmium nitrate to 2.44 barns/D-atom at 2200 m/sec. Figure 4.12 illustrates the geometry for these particular studies.

Prior to analyzing the above measurements, it seemed worthwhile to check Sprevak's model for benzene by comparison to the total cross section σ_T and to any available spectral data for that moderator. The σ_T comparison, described in Section 4.2, was found to be good. An infinite medium thermal neutron spectrum in benzene poisoned to 5.9 barns/H atom with methyl borate was calculated by means of the GATHER code.⁽⁵¹⁾ This calculation is compared to previously measured values⁽⁴⁰⁾ and to the predictions of the Boffi⁽⁵²⁾ model for benzene in Fig. 4.13. At first it appears that Sprevak's model does not give as good agreement with the measurements as does the Boffi model. This is surprising since the angular scattering cross sections are better predicted by Sprevak's model. An attempt was made to determine the cause of the discrepancy by recomputing the spectrum with the Boffi model. Unfortunately, the frequencies and weights listed in Ref. 55 are not consistent and it has not been possible to reproduce the frequency spectrum used in the previous calculations. In addition, the scattering kernel previously generated⁽⁴⁰⁾ could not be found. It was also discovered that the previous calculations⁽⁴⁰⁾ had not accounted for carbon scattering. Moreover, no foil measurements in the benzene experimental studies had been performed so that there was no information on the local leakage. Consequently, the local buckling had been taken as zero in the comparative calculation. Thus it is possible that the agreement between the experimental values and the older calculated data⁽⁴⁰⁾ may have been fortuitous. A new precision spectrum measurement in benzene might be useful in shedding light on this discrepancy.

The agreement of the predictions of Sprevak's model for benzene with observed data seemed to be sufficiently good to proceed to the analysis of the diphenyl studies. First of all, the raw infinite medium measurements were all reduced again using improved mean emission times computed

Fig. 4.12--Geometrical arrangement for spectral measurements at a D₂O - diphenyl measurement

Fig. 4.13--Comparison of experimental and calculated neutron spectra in benzene (5.9 barns/H atom; infinite medium) $B^2=0$

as the first time moment of the flux by the code GATHER.⁽⁵¹⁾ The neutron spectra are compared in Fig. 4.14 to the calculations made with the GATHER code in the B_1 approximation using Sprevak's bound scattering kernel for hydrogen in benzene at 80°C. The agreement is not very good and discrepancies of up to 30% are present. In the past,⁽⁸⁾ the agreement of measured and calculated spectra in an unpoisoned hydrogenous moderator has not been good simply because the leakage effects which dominate the shape of the thermal spectrum here are not treated properly in the B_1 approximation. The calculated neutron spectrum diphenyl shows a very strong dependence on the buckling B^2 for the unpoisoned case. This dependence is significantly lower for the poisoned cases, yet here the agreement is not much, if at all, better. This stands in contrast to the comparison in benzene alone shown in Fig. 4.13. It seems reasonable to ascribe the discrepancies to the use of the benzene kernel for the calculation of diphenyl spectra. However, the possibility cannot be ruled out that some poison has been lost due to evaporation. This possibility has some support by the apparent absence of neutron conservation in the comparison of Fig. 4.14.

It would seem from the above results that the benzene scattering kernel is not adequate for the computation of thermal neutron spectra in diphenyl. Nevertheless, it appeared desirable to perform a preliminary analysis of the spectrum measurements at the D_2O -diphenyl interface rather than wait until a scattering model for diphenyl was developed. The theoretical angular flux at this interface was calculated using the 1DF transport theory code⁽⁵³⁾ in an S_8 representation. Broad group (P_0 and P_1) cross sections were obtained from the GATHER code.⁽⁵¹⁾ These were based on the Sprevak⁽⁹⁾ model for hydrogen in benzene to describe scattering by the diphenyl, and utilized an incoherent scattering model for D_2O based on Haywood's distributed rotational frequency spectrum.⁽⁵⁴⁾ P_0 and P_1 sources from the DSZ code⁽²⁾ were utilized. The experimental and calculated angular fluxes are compared in Fig. 4.15. The agreement is not very good but the discrepancies are consistent with the observations

NEUTRON
FLUX $\times$ ENERGY
(ARBITRARY UNITS)

Fig. 4.14--Neutron spectra in diphenyl at 80°C as a function of poison concentration

Fig. 4.15-- Thermal neutron spectra in the diphenyl-D₂O interface assembly at 80°C

made in the homogeneous studies. The calculated neutron spectra are too hard in the diphenyl and at the interface the peak in the $E\phi(E)$ display is 40% in error. The discrepancy gradually lessens as the distance into the D_2O becomes greater until at Position 8, which is furthest from the interface, the agreement becomes quite fair. This observation is consistent with the good agreement between theory and experiment observed previously in the poisoned D_2O .⁽⁵⁵⁾

5. NEUTRON THERMALIZATION IN ZIRCONIUM HYDRIDE

5.1 INTRODUCTION

The characteristics of neutron scattering by zirconium hydride that make this substance very important as a reactor moderator have been known qualitatively for many years. Recently, intensive efforts have been made in several laboratories to obtain more detailed quantitative information about zirconium hydride properties. Double differential measurements performed at RPI and at Chalk River, reported at the 1967 IAEA symposium at Ann Arbor, (11, 34) have provided a basis for much stricter tests of theoretical models than have formerly been possible, though still greater precision is needed. An important step toward improved knowledge of temperature effects on integral quantities was a series of new measurements at General Atomic of angular scattering at elevated temperatures, reported in Section 5.3. A significant theoretical advance is also represented by the development of a central force lattice dynamical model, described in Section 5.2, that provides a physical explanation for some detailed characteristics of the improved zirconium hydride neutron data now becoming available.

5.2 CENTRAL FORCE MODEL FOR ZIRCONIUM HYDRIDE

Work on a lattice dynamical model for zirconium hydride in which the interatomic forces are restricted to the central type was begun early in 1966 and a preliminary phonon spectrum was obtained.⁽⁶⁾ Since that time, this model has been intensively investigated and calculations have been made of specific heats and neutron scattering cross sections. Much of these results together with a detailed description of the model are now available in a General Atomic topical report.⁽⁵⁶⁾ Here we shall review

the importance of this model and describe qualitatively some of the steps involved in its construction.

Zirconium hydride is an efficient moderator of neutrons with energies in excess of about .14 eV. Such neutrons in collision with hydrogen atoms in the hydride can excite a vibration mode in which the hydrogen atom oscillates about the center of a tetrahedron formed by zirconium atoms. A zeroth approximation to the phonon spectrum for zirconium hydride is thus a simple Einstein oscillator at about .14 eV. More detailed neutron scattering evidence reveals, however, that in fact a continuous distribution of frequencies exists in the vicinity of .14 eV. Fair to good agreement with neutron data has been obtained in calculations based on a phenomenological phonon spectrum consisting of a Debye spectrum cut off at .02 eV plus a Gaussian centered at .137 eV with a full width at half maximum of .02 eV.⁽⁵⁷⁾ For several reasons, there has been a need to understand the success of this phenomenological model in terms of a quantitative lattice dynamical description. For example, hydrogen-hydrogen interactions in the lattice are a plausible explanation for the broadening of the optical part of the phonon spectrum, but proof was needed that the observed width could, in fact be accounted for by assuming a force of reasonable magnitude. Also, a lattice dynamical model was needed to provide in neutron scattering calculations the relative weighting of acoustical to optical modes, which was chosen somewhat arbitrarily in calculations based on the phenomenological model.⁽⁵⁷⁾

To obtain the frequencies and eigenvectors needed for the lattice dynamical phonon spectrum and for neutron scattering calculations, the dynamical matrix for the ZrH_2 lattice was obtained as a function of wave vector $\vec{q}$, retaining forces out to third nearest neighbors in the case of hydrogen and second nearest neighbors for zirconium. A code, ELSC,⁽⁵⁶⁾ was written to calculate this dynamical matrix at a set of $\vec{q}$ points evenly distributed throughout the irreducible element of the first Brillouin zone.

The code utilizes a UNIVAC 1108 subroutine to diagonalize the dynamical matrix, thus obtaining both the eigenvalues and the eigenvectors corresponding to each $\vec{q}$ - point. Appropriate frequency distributions are then constructed from the calculated sets of frequencies and eigenvectors. Considerable effort was required both to insure an evenly distributed set of $\vec{q}$ points for root sampling and to utilize lattice symmetries effectively to cut down the running time of the code, which in its original version required the evaluation and diagonalization of an 18 by 18 matrix for each $\vec{q}$ point. A recent simplified version cuts this matrix to a 9 by 9 array and makes possible calculations with 3500 $\vec{q}$ points (31,500 frequencies) in about 6 minutes on the UNIVAC 1108 computer.

The phonon spectra obtained from ELSC results were used first to calculate values of the specific heat of ZrH_2 as a function of temperature. Comparisons with the data⁽⁶⁴⁾ guided the selection of the Zr-Zr force constant, to which the acoustical modes affecting the low-temperature specific heat are particularly sensitive. The H-H and Zr-H force constants were selected to give a position and width for the optical distribution comparable to that of the Gaussian model described above. Considerable structure in the one-phonon double differential scattering cross section is predicted by the new model, but the data are not yet sufficiently precise to provide a good test of these predictions. Nevertheless, over-all agreement with neutron data - both integral and differential - and, particularly, agreement with specific heat data indicates that the central force model represents a distinct improvement over previous phenomenological models. Figure 5.1 shows the results of a neutron spectrum calculation based on the new model in comparison with the Gaussian-plus-Debye model. Some improvement in agreement is noticeable; however, the change is not so evident as that seen in double differential cross section comparisons.⁽⁵⁶⁾ As more precise neutron data become available, it will be possible to improve the model by readjusting the force constants and using ELSC to

Fig. 5.1--Infinite medium neutron spectrum in borated $\text{ZrH}_{1.75}$

compute a new frequency spectrum, following the method described in Ref. 56. Data have very recently become available which indicate structure in the acoustic modes⁽³⁴⁾ and an asymmetry in the optical distribution,⁽¹¹⁾ which is in accord with central force model predictions. Further comparisons between theoretical results and experimental data, both integral and differential, are in progress.

5.3 ANGULAR SCATTERING BY ZIRCONIUM HYDRIDE AT ELEVATED TEMPERATURES

Data reduction of angular scattering measurements^(43, 44) has been completed. These measurements, using a .145-inch thick pressed disc of $\text{ZrH}_{1.85}$, were made at room temperature and at 700°K over a range of angles from 20° to 155°. Energies from .008 eV to 1 eV were measured using the time-of-flight technique. A new type sample holder was designed and constructed. This sample holder, seen in Fig. 5.2, employs stainless steel knife edge seals and aluminum windows. Results of a series of sample transmission measurements made before and after heating showed that there was a negligible change in the sample composition at high temperature. Because of the relative thickness of the sample used (.145 inch), the multiple scattering correction factors were believed to be the most important corrections to the measurements. The computer code MUSE⁽⁴⁵⁾ was used to calculate the corrections over an energy mesh and angular range covering the experimental energy and angle points. The results of these calculations are shown in Figs. 5.3 and 5.4 for a few angles at two temperatures.

A comparison of thick sample to thin sample scattering at room temperature was made to check the multiple scattering correction methods. The two sample thicknesses used were .040 inch and .145 inch, which gave transmissions of 0.89 and 0.64 respectively at 0.1 eV. The comparison is given in Fig. 5.5 and the agreement is reasonable. This agreement, from two independent measurements and two different thicknesses using

Fig. 5.2--Zirconium hydride sample holder used at elevated temperatures

Fig. 5.3--Calculated multiple scattering correction factor for single differential scattering by zirconium hydride at 296° K

Fig. 5.4--Calculated multiple scattering correction factor for single differential scattering by zirconium hydride at 700° K

Fig. 5.5--Comparison of measured angular scattering cross sections of zirconium hydride at 296° K for two different sample thicknesses

the same method for multiple scattering correction, is an indication (though not entirely conclusive - see Section 2.4) that this method yields reasonable results when used for thick samples. The theoretical value of the single differential cross section, as calculated from the Gaussian-plus-Debye-model, ^(19, 57) is also shown and the agreement with measurement is seen to be good except near the oscillator levels. This area of disagreement is common to both thicknesses.

The experimental data have all been corrected for multiple scattering and have been normalized to the theoretical total cross section. The angular scattering cross section measurements at 700°K are compared to theory for a few selected energies in Fig. 5.6. The agreement between experiment and theoretical predictions from the Gaussian-plus-Debye model is good. The average statistical error at each point is less than 1%. Since there was some monitor drift, a maximum error of 3% has therefore been assigned to each point. The corresponding error bars would, however, be included in the size of the points in Fig. 5.6. The change in the angular scattering cross section with temperature is shown in Fig. 5.7 for a scattering angle of 155°. Changes of up to 20% are predicted by the Gaussian-plus-Debye model and are observed in the measured data. Again the agreement of experiment and calculation is seen to be good except near the oscillator levels.

In general, it appears that the present scattering model used for zirconium hydride is fairly satisfactory for describing single-differential results and these observations support the same conclusions reached in infinite medium spectral measurements. ⁽⁵⁷⁾ Theoretical predictions from the new central force model ⁽⁵⁸⁾ for single differential angular scattering do not differ greatly from the predictions of the Gaussian-plus-Debye model. Preliminary results show a maximum difference of about 2% in the area of the oscillator levels. This difference could not be seen in this experiment.

Fig. 5.6--Angular scattering cross section of zirconium hydride at 700°K

Fig. 5.7--Comparison of angular scattering cross sections of zirconium hydride for different temperatures

6. NEUTRON THERMALIZATION IN Be AND BeO

6.1 INTRODUCTION

Some time ago a scattering kernel for beryllium⁽¹²⁾ was developed by using the incoherent and isotropic approximations. This kernel appears satisfactory for predicting position dependent thermal neutron spectra for room temperature and for higher temperatures. For spectra at liquid nitrogen temperatures, however, this kernel shows some disagreements with experiment (Section 6.3). Part of this error is undoubtedly due to inelastic coherent effects. It has been thought advisable to try to compute the lattice dynamics of beryllium from first principles, to see if it is indeed possible at this stage to make calculations independent of experiment. Next year's program will include a rewriting and speed-up of the machine code COIN⁽¹⁴⁾ so that one-phonon coherent inelastic effects can be included in our calculations of the scattering cross section.

6.2 FIRST PRINCIPLES CALCULATION OF PHONON DISPERSION CURVES IN BERYLLIUM METAL

In the previous Annual Progress Report⁽⁶⁾ we have outlined a method of calculating phonon dispersion curves from first principles for a metal crystallizing in a nonprimitive lattice. The method was then applied to the case of beryllium, which has the hexagonal closed packed structure. In the same reference we also reported numerical results for the phonon dispersion curves obtained with a crystal potential given by Loucks and Cutler⁽⁶⁰⁾ and a free electron approximation for the dielectric screening.

This year we have turned to the numerical evaluation of the true dielectric matrix $\epsilon(q + G, q + G')$ as defined in Ref. (6). This requires

a prior knowledge of the band structure for beryllium. Although several such calculations are reported in the literature, none of them actually provides the wave functions, i. e., the Bloch states which are required in the expression for ϵ . Hence, a code called SYMP was written which calculates band energies and wave functions by the well known method of orthogonalized plane waves (OPW). This information is then put on a tape which serves as input to a second code called XELT, which calculates the dielectric matrix for any direction of the phonon wave vector q . Calculations along the (0001) axis have been performed with 11, 23, and 37 OPW and the results are compared to the free electron dielectric constant in Figs. 6.1, 6.2, and 6.3. The curves actually represent the diagonal elements of the matrix

$$\chi(q + G, q + G') = \left[\alpha(q + G, q + G') - \delta_{GG'} \right] \frac{\Omega}{4\pi e^2} \frac{|q+G|^2}{f(|q+G|^2)} \quad (6.1)$$

for $q + G$ along the (0001) direction. In this expression, G is a reciprocal lattice vector, Ω is the unit cell volume, e the charge of the electron and f is an exchange factor, defined as

$$f(X) = 1 - \frac{1}{2} \frac{X^2}{X^2 + k_F^2 + k_s^2} \quad (6.2)$$

where k_F is the Fermi momentum and k_s the Fermi Thomas screening constant. One of the difficulties encountered in the calculation of ϵ was the correct evaluation of the principal value in the expression for χ

$$\begin{aligned} \chi(q + G, q + G') = & -\frac{1}{N} \sum_{kk'} \frac{n(k) - n(k')}{E(k) - E(k')} \langle \psi_k | e^{-i(q+G) \cdot r} | \psi_{k'} \rangle \\ & \cdot \langle \psi_{k'} | e^{i(q+G') \cdot r} | \psi_k \rangle \end{aligned} \quad (6.3)$$

Fig. 6.1--Comparison of diagonal elements of $\chi(\vec{q}+\vec{G}, \vec{q}+\vec{G})$ as calculated with 11 OPW to the dielectric constant of an electron gas:

Fig. 6. 2--Dielectric function for beryllium

Fig. 6.3--Diagonal terms of the screening matrix for 37 OPW

where ψ_k is a Bloch state with energy $E(k)$ and $n(k)$ is the corresponding occupational number.

For k' approaching k we have

$$\lim_{k' \rightarrow k} \frac{n(k) - n(k')}{E(k) - E(k')} = \frac{dn}{dE} = \delta(E - E_F) \quad (6.4)$$

where E_F is the Fermi energy. In order to find the correct contribution from the infinitesimal interval about E_F we separated the contributions from the region

$$E_F - \Delta < E(k) < E_F + \Delta \quad (6.5)$$

with $\Delta = .05$ Rydbergs. In this narrow interval, we approximated the occupational number (for $T = 0^\circ K$)

$$\begin{aligned} n(k) &= 1 \quad \text{for} \quad E(k) \leq E_F \\ &= 0 \quad \text{for} \quad E(k) > E_F \end{aligned} \quad (6.6)$$

by the linear function

$$n(k) = 1 - \frac{E(k) - E_F + \Delta}{2\Delta} \quad (6.7)$$

For $E(k)$ and $E(k')$ within the interval (6.5) we then get

$$\frac{n(k) - n(k')}{E(k) - E(k')} = -\frac{1}{2\Delta} \quad (6.8)$$

With the dielectric constant obtained from the 37 OPW calculation, we have determined the phonon dispersion curves for the (0001) direction. Only diagonal elements of the dielectric constant were retained. Because of the large truncation errors, it was necessary to extrapolate ϵ beyond the outermost shell in reciprocal space using its expression for free electrons. In Fig. 6.4 we compare the results of this calculation with Schmunk's experimental data and the previously reported results using a free electron dielectric constant. It was hoped that the more sophisticated calculation

Fig. 6.4--Phonon dispersion curves for beryllium
for the (0001) direction

would lead to improved agreement with experiments, but unfortunately this has not been borne out by the results obtained so far. As is seen in Fig. 6.4, the slope of the experimental acoustical branches at small q values (i. e., the velocity of sound) is better reproduced by the free electron model. Apparently, this discrepancy in the initial slope is due to the dip of the dielectric constant at low values of q , since excepting the very low q range, the 37 OPW and the free-electron dielectric constants are very close to each other. It is possible however, that the dip in ϵ should be narrower than the one shown in Fig. 6.3 and that our treatment of the principal value mentioned above leads to such an error due to an excessively wide sampling interval Δ (see Eq. 6.5). This possibility will be investigated in the future, as well as the influence of the off-diagonal terms of $\epsilon(q+G, q+G')$, which so far have been neglected.

6.3 THERMAL NEUTRON SPECTRA IN BERYLLIUM AT 77.4°K

Spectral measurements in beryllium metal at liquid nitrogen temperature (77.4°K) were performed to test the adequacy of Young's⁽¹²⁾ bound scattering kernel for beryllium at this temperature. This kernel is based on the inelastic incoherent scattering approximation. It was suspected that this approximation might not be appropriate at 77.4°K and that interference scattering would need to be considered. The problem is relevant to the use of beryllium as a reflector in the ROVER nuclear rocket reactor. Hopefully, improved understanding of thermalization in cold beryllium would allow more accurate prediction of the core-reflector interface power peaking in that reactor.

The spectral measurements were performed by the usual time-of-flight means⁽¹⁻⁶⁾ using the General Atomic LINAC. The geometry for the measurement is illustrated in Fig. 6.5. A stack of beryllium 19.64 in. high by 21.77 in. long by 17.26 in. wide was placed in a double walled aluminum tank into which liquid nitrogen was introduced. The beryllium was poisoned to 0.25 barns/Be atom by borated stainless steel foils 5 mils thick placed at every half inch. The poisoning reduced the dependence of

Fig. 6.5 -- Configuration for spectral measurements in Be at 77.4°K

the spectrum on leakage and made the geometry more amenable to analysis by a one-dimensional transport theory code. The tank was surrounded by 4 in. of styrofoam for insulation purposes. One inch of iron on the side nearest the source helped to spread the neutrons and better approximate an incident plane-wave source.

The temperature of the blocks was monitored at various positions and maintained within 3°C of liquid nitrogen boiling point (77.4°K). Dry nitrogen was fed into the assembly to prevent air diffusing in and resultant ice formation. Spatial measurements were made in a direction perpendicular to the source-assembly axis at the positions indicated in Fig. 6.5. The spatial dependence was obtained by inserting blocks of beryllium and borated stainless steel to the desired measured position. The front of the reentrant hole was covered with a 1-mil layer of aluminum foil on which air was blown to prevent icing up.

Flux plots were made in the beryllium assembly with various foils in three mutually perpendicular directions to determine the local buckling at the spectral measurement positions and to derive a basis for the slowing-down source distribution. These plots were performed at room temperature due to limitations in the system design. The distributions in the vertical and horizontal directions closely approximated a cosine dependence. The distributions in the axial direction are shown in Fig. 6.6. Edge effects did not appear to be significant at the measurement position of 27.9 cms; in addition, the slopes of the two curves at that position were similar, indicating that diffusion theory would adequately describe the leakage in that axial direction.

The theoretical neutron spectra were calculated using the 1DFtransport theory code⁽⁵³⁾ in an S_{16} approximation. This is a one-dimensional code and the axis of the measurement positions was chosen as the calculational direction. Broad group cross sections (P_0 and P_1) were obtained using the averaging procedures of the GATHER code.⁽⁵¹⁾ The scattering kernel was generated by FLANGE⁽⁶¹⁾ from the scattering law output of

Fig. 6.6--Spatial foil activities in the beryllium assembly
(Axial Distribution)

GASKET.⁽⁷⁾ The latter code computed the scattering law in the inelastic incoherent approximation utilizing a frequency spectrum based on Young's central force model for beryllium.⁽¹²⁾ Coherent elastic scattering was calculated by means of the code HEXSCAT⁽⁶²⁾ and this was combined with the FLANGE output when a library cross section tape was made. The broad group cross sections were modified by the addition of a $D(E)B^2$ term to the absorption and total cross sections. In this term the B^2 was obtained from Cd(In) flux plots normal to the direction of the calculation. The flux plot in the calculational direction was utilized in the DSZ code⁽²⁾ to compute a P_0 and P_1 slowing down source for use in IDF.⁽⁵³⁾ The calculation was made assuming symmetry across the beryllium stack so that reflective boundary conditions and half-region representation could be utilized to minimize computer memory requirements.

The theory is compared to the experiment in Fig. 6.7. The only normalization is made in the $1/E$ range of the central position (No. 1) so that an intensity as well as shape comparison can be made. The angular fluxes in the figure have been multiplied by arbitrary numbers for display purposes only. The agreement at the central position (No. 1) is quite reasonable except at low energies where coherent scattering effects made the broad group cross sections a little questionable. This is evident at the surface position (No. 5) where the measured flux shows considerably more structure than in the calculations. The outward going flux near the assembly edge shows a peak at low energies and the inward going flux shows a dip; this was observed in previous room temperature measurements.⁽⁶³⁾ The agreement of theory and measurement is not very good. Much of the difference is due to intensity discrepancies. At the surface, for instance, the shape of experimental and theoretical curves are similar though the intensity is in error by a factor of $\sim 50\%$. These discrepancies are believed to be due to the following:

1. The source distribution used in the calculation was based on room temperature flux plot measurements in the experimental

Fig. 6.7--Thermal neutron spectra in poisoned beryllium (0.25 barns/Be atom at 2200 in/sec) at 77.4°K

assembly. The absence of the LN_2 may have affected the distribution.

2. The poisons in the beryllium (borated stainless steel) were treated as $1/v$ absorbers plus constant scatterers. This could lead to discrepancies at low energies where beryllium cross sections are very small.
3. The coherent scattering is singular and it might be necessary to include scattering moments higher than P_1 , particularly for the surface calculation. The GATHER code,⁽⁵¹⁾ however, does not provide for averaging the higher moments.
4. The angular flux is very peaked near the edge of the assembly and a representation of higher order than S_{16} might be necessary to improve the agreement of theory and measurement.

Generally, the shape agreement of theory and experiment is fair; at the center it is quite good. Thus the energy transfer cross sections of the beryllium kernel appears to be predicted reasonably well. We can then say that the incoherent approximation appears to be adequate for beryllium even at 77.4°K .

It is interesting to note that if a neutron is scattered below the Bragg cutoff, it has a very high probability of leaking out of the assembly. Upscattering is very small so that the thermal peak of the spectrum does not shift very much with temperature. This is illustrated very well in Fig. 6.8 which compares the room temperature spectrum measurement in a similar poisoned Be assembly to the values at the corresponding central position at 77.4°K . The thermal peak shifts from 0.035 eV at 296°K to 0.032 eV at 77.4°K ; this change is very much smaller than the relative change in the absolute temperature.

6.4 SCATTERING KERNEL FOR BeO

A model for the lattice dynamics of beryllium oxide based on the assumption that the crystal is ionic has been developed.⁽¹⁵⁾ The scattering cross section was computed based on this model, but we do not feel

Fig. 6.8--Variation of thermal neutron spectrum in beryllium with temperature

that it is significantly better than the Debye model which is already on the ENDF system tape. A better treatment of the balance forces in the crystal is needed to give a more realistic model of the lattice dynamics. This greatly complicates the problem, but perhaps there is enough infrared data available to allow an evaluation of the force constants. In Fig. 6.9 we show the total cross section of BeO compared to experiment. Unfortunately, there are little other data. While the purely ionic model does not agree well with the dispersion curve measurements of Brugger,⁽⁶⁴⁾ it is still possible that the model will give good agreement with integral neutron data. The conclusion we draw here is that the Debye model for BeO predicts infinite medium spectra fairly well,⁽⁵⁾ and the ionic crystal model also should predict infinite medium spectra satisfactorily, but a good deal more work remains to be done in order to have a completely satisfactory scattering kernel for BeO.

Fig. 6.9--Total cross section of beryllium oxide

7. SCATTERING LAWS FOR UC AND UO_2

7.1 INTRODUCTION

Scattering kernels for both UO_2 and for UC have been calculated by using the incoherent and isotropic approximations which allow the cross sections to be expressed in terms of the phonon spectrum of the lattice vibrations.⁽⁶⁵⁾ In our first effort at calculating the cross sections for these moderators, we used Debye frequency spectra with the Debye temperatures chosen by fitting to the observed specific heat. These kernels are not expected to yield very good agreement when compared to measured neutron spectra, however, it was considered worthwhile to use such calculations until more sophisticated computations are done.

For UO_2 , at least, it is possible to make a much more precise calculation of the scattering kernel than that given by the Debye model. Measurements of the dispersion curves of UO_2 by Dolling et al.,⁽⁶⁶⁾ have been fitted by a shell model⁽⁶⁷⁾ of the lattice dynamics, under the assumption that the short range forces only act between nearest neighbors of both alike and non-alike atoms. UO_2 has a strong ionic character, leading to long range forces. Using this model of the lattice dynamics, we can obtain the frequencies and eigenvectors necessary to calculate the neutron scattering cross section in the incoherent approximation. It is necessary to compute the scattering from the oxygen atom separately from the uranium atoms, which greatly complicates the numerical work in this problem. This work is described more fully in Section 7.3.

The moderator UC is much more complicated since it exists in different allotropic forms and does not form a simple crystal. Consequently,

it is not understood at present how to proceed towards computing a more accurate scattering kernel. The recently published neutron scattering data on UC and UO_2 from RPI⁽¹¹⁾ is expected to guide this research.

7.2 SCATTERING LAWS FOR UO_2 AND UC

Scattering laws for UC and UO_2 are of interest for the design of certain types of thermal reactors. It appears that the magnitude and sign of the computed prompt temperature coefficient is sometimes sensitive to the choice of treating the light atom in these fuels as either completely bound or completely free. To assist in these calculations we have computed the scattering laws for bound carbon in UC and bound oxygen in UO_2 using the Debye approximation.

The serious limitations of the Debye approximation should be pointed out so that these scattering laws will be used with caution. Basically, the Debye approximation rests on the assumption that the velocity of phonons in a lattice is independent of the phonon energy and direction of travel. This assumption, which is certainly accurate for very low energy vibrations of long wavelength, leads to a density of phonon states, $\rho(\omega)$, proportional to ω^2 , where $\hbar\omega$ denotes the energy of the phonon. This distribution must be cut off at some maximum frequency ω_D , selected such that $\int_0^{\omega_D} \rho(\omega) d\omega$ equals the total number of states. This arbitrary cutoff at ω_D , known as the "Debye frequency" is certainly not physical. Moreover, there is no reason to suppose that the frequency spectrum for an actual lattice will follow the ω^2 form except at very low frequencies. For example, it is possible that peaks will occur in the frequency spectrum at relatively high energies due to vibrational modes associated with the lattice symmetry. Such high frequency or optical states have a significant effect on the shape of the specific heat as a function of temperature. The presence of such vibrational states also has a profound effect on the neutron scattering. A simple Debye model cannot possibly describe even qualitatively such lattice dynamical effects.

The code GASKET⁽⁷⁾ was used to compute the inelastic incoherent scattering law for carbon in UC and for oxygen in UO₂. The phonon spectrum $\rho(\omega)$ was a Debye spectrum, i. e.,

$$\rho(\omega) \propto \omega^2 \quad (7.1)$$

and the cutoff was adjusted to match the observed specific heats. The cutoff frequency ω_D or Debye temperature was obtained in the following way: the specific heat at constant volume C_V is related to the true normalized frequency spectrum $\rho(\omega)$ by

$$\frac{C_V}{3R} = \int_0^{\omega_D} \rho(\omega) \left(\frac{\omega}{T} \right)^2 \frac{e^{\omega/T}}{[e^{\omega/T} - 1]^2} d\omega \quad (7.2)$$

where R is the universal gas constant and T is the temperature. We have computed $C_V/3R$ for a range of ω_D and T and the resultant behavior is shown in Fig. 7.1. The observed specific heat is measured at constant pressure and we must compute C_V from

$$C_V = C_P - \frac{9\beta^2 T}{K} \quad (7.3)$$

where β is the temperature coefficient of linear expansion, and K is the compressibility,

$$K = \frac{1 - 2\nu}{E} \quad (7.4)$$

where E is Young's Modulus and ν is Poisson's ratio.

Fig. 7.1--Variation of $CV/3R$ with cutoff frequency and temperature for a Debye model

The data given in Table 7.1 were used to compute ω_D at room temperature, using the equations given above. For UO_2 , the observed specific heat data⁽⁶⁸⁾ appeared to be consistent and reasonable though the possibility of vibrational states at energies too high to affect the specific heat could not be excluded. The specific heat data for UC was found to consist of only two points⁽⁶⁹⁾ and in the absence of confirming information must be treated with more reservation. It is worth noting that other values of C_p for UC in the literature⁽⁷⁰⁾ are reported elsewhere⁽⁷¹⁾ as observed values, but are in fact calculated values and are useless for our purposes.

At higher temperatures ω_D could not be computed properly, since for both UC and UO_2 the value of $C_V/3R$ was too close to the theoretical limit of 1.00. Thus, scattering law calculations based on the Debye model were performed only for room temperature, while a free gas model was used to describe the scattering at higher temperatures.

The calculation of the room temperature Debye-model scattering law proved to be a substantial undertaking, because of numerical problems encountered in the computation. The original α , β mesh used was a 50×80 matrix having $\Delta\alpha = 0.25$ up to $\alpha = 3.0$ and $\Delta\beta = 0.15$ up to $\beta = 4.0$, the values above that increasing geometrically. It was found that the computed $\log S$ was not linear for low α and the methods for low α treatment incorporated in FLANGE⁽⁶¹⁾ gave dubious results for various integral quantities. The data were therefore regenerated using an α mesh of 80 points with $\Delta\alpha = 0.05$ up to $\alpha = 0.6$. The same β mesh was used. This was found to be satisfactory.

An integral check of the computed $S(\alpha, \beta)$ was then made by utilizing FLANGE to calculate the inelastic σ_0 and σ_1 and ELAST⁽⁷⁵⁾ to compute the elastic σ_0 and σ_1 . The total σ_0 and σ_1 cross sections for UC were bad but $\bar{\mu}$ between 0.1 and 0.2 eV was even worse.

Table 7.1
REFERENCE PHYSICAL DATA OF UC AND UO₂

Quantity	UC ^(69, 71, 73)	UO ₂ ⁽⁷²⁾
β	$1.03 \times 10^{-5}/^{\circ}\text{C}$	$1.03 \times 10^{-5}/^{\circ}\text{C}$
T	300 ^o K	300 ^o K
E	25×10^6 psi	26×10^6 psi
ν	0.29	0.3
Cp	1.935 ergs/gm - ^o C	0.058 cal/gm - ^o K
ω_D (Calculated)	0.0332 eV	0.051 eV

The energy mesh used was suspected of leading to numerical integration problems and a new energy mesh of 99 ΔE s was therefore constructed. The minimum ΔE in the new mesh was larger than before, but ΔE was half as large as the previous values used between 0.1 and 0.2 eV. The new calculated total σ_0 and σ_1 and $\bar{\mu}$ were improved in this energy range but $\bar{\mu}$ was poor at higher energies, where ΔE ranged from 0.015 to 0.03 eV. Since $S(\alpha, \beta)$ drops quite sharply at $\beta = \omega_D/T$, it was concluded that a fine energy mesh is needed when utilizing a Debye model or significant contributions may be lost when integrating over energy. It should be noted that for the above meshes the inelastic σ_0 and σ_1 and $d\sigma/dE$ were fairly smooth. The calculation of $\bar{\mu}$ appeared to provide a more severe integral check. The problem was more pronounced with UC because its Debye temperature was taken as 0.0332 eV, which is much lower than the value taken for UO₂ of 0.051 eV. For practical purposes, the energy mesh used in FLANGE should be smaller than $\omega_D/4$. The final calculation of scattering law data utilized an energy mesh satisfying this last condition.

7.3 CENTRAL FORCE MODEL FOR UO_2

In this section, we discuss a shell model for UO_2 that has been fitted to the dispersion curve measurements of Dolling, Cowley and Woods.⁽⁶⁶⁾ We shall call this model a central force model, although in the literature there seems to be some confusion in terminology on this point with the so-called axially symmetric or A-S model of Lehman, et al.⁽⁷⁶⁾

First let us consider a two-body potential $\varphi(R)$ which depends only on the distance between two atoms, and allow a small displacement

$$\Delta S = |\vec{R} + \Delta\vec{R}| - |\vec{R}|; R = |\vec{R}|, \varphi[|\vec{R} + \Delta\vec{R}|] = \varphi[R + \Delta S], R = |\vec{R}| \quad (7.5)$$

Now

$$\Delta S = |\vec{R} + \Delta\vec{R}| - |\vec{R}| = \frac{\vec{R} \cdot \Delta\vec{R}}{R} + \frac{(\Delta R)^2}{2R} - \frac{1}{2} \frac{|\vec{R} \cdot \Delta\vec{R}|^2}{R^3} \quad (7.6)$$

$$\varphi[S + \Delta S] = \varphi(R) + \Delta S \frac{\partial \varphi}{\partial R} + \frac{1}{2} (\Delta S)^2 \frac{\partial^2 \varphi}{\partial R^2} + \text{higher order terms.} \quad (7.7)$$

This expansion of the potential is equivalent to the A-S model but as we have seen is derived from an assumption of central forces. What is usually called the central force model would be obtained if $\frac{1}{R} \frac{\partial \varphi}{\partial R} = 0$, and is equivalent to having a lattice with springs attached to all pairs of atoms, and such that the springs are relaxed when the lattice is in equilibrium. Solid argon for example would have the terms in $\frac{\partial \varphi}{\partial R}$ present, and so we believe the A-S model, or what we prefer to call the central force model is more realistic than what we shall call the spring model, $\frac{\partial \varphi}{\partial R} = 0$. There is one subtle point however, which is that if the force constants are given arbitrary values for different shells of atoms about the origin, then the A-S model is not a true central force model unless we allow completely arbitrary potential forms. We also see that central forces lead to bond bending as well as bond stretching forces.

For the shell model⁽⁶⁷⁾ we take the short range forces between core-shell, shell-shell and core-core to be the same except for the shell-core constant in the same atom which is determined from the ionic polarizability.

UO₂ has the fluorite structure with the lattice vectors given by

$$\vec{a}_1 = \frac{a}{2} (0, 1, 1), \quad \vec{a}_2 = \frac{a}{2} (1, 0, 1), \quad \vec{a}_3 = \frac{a}{2} (1, 1, 0). \quad (7.8)$$

The positions of the atoms in a unit cell are

$$\vec{x}_u = 0, \quad \vec{x}_{01} = \frac{a}{4} (1, 1, 1), \quad \vec{x}_{02} = \frac{a}{4} (1, 1, 1). \quad (7.9)$$

The lattice spacing a is $5.469 \text{ \AA}$, and the volume of a unit cell is $a^3/4$.

If we associate the triad (ℓ_1, ℓ_2, ℓ_3) with a lattice vector

$$\mathbf{x}(\ell) = \ell_1 \vec{a}_1 + \ell_2 \vec{a}_2 + \ell_3 \vec{a}_3, \quad (7.10)$$

then we have for the nearest neighbors of 02 in the zero cell ($\ell_1 = \ell_2 = \ell_3 = 0$).

01: $(-1, -1, 0); (-1, 0, 0); (0, -1, 0); (0, 0, -1); (0, -1, -1); (-1, 0, -1)$.

U: $(0, 0, 0), (-1, 0, 0), (0, -1, 0), (0, 0, -1)$

The nearest neighbors of 01:

02: $(1, 1, 0), (1, 0, 0), (0, 1, 0), (0, 0, 1), (0, 1, 1), (1, 0, 1)$

U: $(0, 0, 0), (1, 0, 0), (0, 1, 0), (0, 0, 1)$

The nearest neighbors of U

02: $(0, 0, 0); (1, 0, 0); (0, 1, 0); (0, 0, 1)$

01: $(0, 0, 0); (-1, 0, 0); (0, -1, 0); (0, 0, -1)$

U: $(1, 0, 0); (-1, 0, 0); (0, 1, 0); (0, -1, 0); (0, 0, -1); (0, 0, 1);$

$(1, -1, 0); (0, 1, -1); (-1, 1, 0); (1, 0, -1); (0, -1, 1); (-1, 0, 1).$

For the short range potential we write

$$\Phi = \frac{1}{2} \sum_{\ell, \ell', K, K'} \Phi(|\vec{X}_K^{\ell} + \vec{U}_K^{\ell} - \vec{X}_{K'}^{\ell} - \vec{U}_{K'}^{\ell}|) \quad (7.11)$$

where Φ is the sum then of all two-body potentials.

The dynamical matrix is given by

$$R_{\alpha\beta}^{(q)}(KK') = e^{i\vec{q} \cdot (\vec{X}(K') - \vec{X}(K))} \sum_{\ell} \frac{\partial^2 \Phi}{\partial U_{\alpha}^{(0)}(K) \partial U_{\beta}^{\ell}(K')} \bigg|_{\vec{U} = 0} e^{i\vec{q} \cdot \vec{X}(\ell)}$$

$$\varphi(R + \Delta R) = \varphi(R) + \frac{\vec{R} \cdot \Delta \vec{R}}{R} \frac{\partial \varphi}{\partial R} + \frac{(\Delta R)^2}{2R} \frac{\partial^2 \varphi}{\partial R^2} - \frac{1}{2} \frac{(\vec{R} \cdot \Delta \vec{R})^2}{R^3} \frac{\partial^2 \varphi}{\partial R^2} + \frac{1}{2} \frac{(\vec{R} \cdot \Delta \vec{R})^2}{R^2} \frac{\partial^2 \varphi}{\partial S^2} \quad (7.12)$$

+ higher order terms in $\Delta \vec{R}$ which are neglected for this discussion.

Now we observe that

$$\begin{aligned} R^2 (\Delta R)^2 - (\vec{R} \cdot \Delta \vec{R})^2 &= R^2 (\Delta R)^2 (1 - \cos^2(\vec{R}, \Delta \vec{R})) \\ &= R^2 (\Delta R)^2 \sin^2(\vec{R}, \Delta \vec{R}) = (\vec{R} \times \Delta \vec{R})^2, \end{aligned} \quad (7.13)$$

so that

$$\varphi(S + \Delta S) = \varphi(R) + \frac{\vec{R} \cdot \Delta \vec{R}}{R} + \frac{\partial \varphi}{\partial R} + \frac{(\vec{R} \times \Delta \vec{R})^2}{2R^2} \left(\frac{1}{R} \frac{\partial \varphi}{\partial R} \right) + \frac{(\vec{R} \cdot \Delta \vec{R})^2}{2R^2} \frac{\partial^2 \varphi}{\partial R^2} \quad (7.14)$$

where $\vec{U}_K^{\ell}$ is the small displacement of the Kth atom in the ℓ -th unit cell of the crystal and q is the phonon wave-vector. The full expression for $R_{\alpha\beta}^{(q)}(KK')$ is then

$$\begin{aligned}
R_{\alpha\beta}^{(q_{KK'})} = & e^{i\vec{q} \cdot (\vec{X}(K') - \vec{X}(K))} \sum_{\ell} \left[-\frac{\partial \Phi}{\partial R} \frac{\delta_{\alpha\beta}}{|\vec{X}(K) - \vec{X}(\ell_{K'})|} \right. \\
& + \frac{\partial \Phi}{\partial R} \frac{(X_{\alpha}(K) - X_{\alpha}(\ell_{K'}))(X_{\beta}(K) - X_{\beta}(\ell_{K'}))}{|\vec{X}(K) - \vec{X}(\ell_{K'})|^3} \\
& \left. - \frac{\partial^2 \Phi}{\partial R^2} \frac{(X_{\alpha}(K) - X_{\alpha}(\ell_{K'}))(X_{\beta}(K) - X_{\beta}(\ell_{K'}))}{|\vec{X}(K) - \vec{X}(\ell_{K'})|^2} \right] e^{i\vec{q} \cdot \vec{X}(\ell)} \\
& + \delta_{KK'} \sum_{\ell_{K''}} \left[\frac{\partial \Phi}{\partial R} \frac{\delta_{\alpha\beta}}{|\vec{X}(K) - \vec{X}(\ell_{K''})|} \right. \\
& - \frac{\partial \Phi}{\partial R} \frac{(X_{\alpha}(K) - X_{\alpha}(\ell_{K''}))(X_{\beta}(K) - X_{\beta}(\ell_{K''}))}{|\vec{X}(K) - \vec{X}(\ell_{K''})|^3} \\
& \left. + \frac{\partial^2 \Phi}{\partial R^2} \frac{(X_{\alpha}(K) - X_{\alpha}(\ell_{K''}))(X_{\beta}(K) - X_{\beta}(\ell_{K''}))}{|\vec{X}(K) - \vec{X}(\ell_{K''})|^2} \right] \quad (7.15)
\end{aligned}$$

We now define force constants in the following manner:

$$\frac{\partial^2 \Phi}{\partial R^2} = \frac{e^2}{V_c} A_1, \quad \frac{1}{R} \frac{\partial \Phi}{\partial R} = \frac{e^2}{V_c} B_1, \quad \text{for uranium-oxygen 1 or 2} \quad (7.16)$$

$$\frac{\partial^2 \Phi}{\partial R^2} = \frac{e^2}{V_c} A_2, \quad \frac{1}{R} \frac{\partial \Phi}{\partial R} = \frac{e^2}{V_c} B_2, \quad \text{for oxygen 1 - oxygen 2} \quad (7.17)$$

$$\frac{\partial^2 \Phi}{\partial R^2} = \frac{e^2}{V_c} A_3, \quad \frac{1}{R} \frac{\partial \Phi}{\partial R} = \frac{e^2}{V_c} B_3, \quad \text{for uranium-uranium} \quad (7.18)$$

Thus, in units of e^2/V_c we can calculate the elements of the short range dynamical matrix:

for Uranium-Uranium:

$$R_{\alpha\alpha} = \frac{8}{3} (A_1 + 2B_1) + 2(A_3 + B_3) (2 - \cos \pi q_\alpha (\cos \pi q_\beta + \pi q_\gamma)) \\ + 4 B_3 (1 - \cos \pi q_\beta \cos \pi q_\gamma) \quad (7.19)$$

for the diagonal components, and

$$R_{\alpha\beta} = 2(A_3 - B_3) \sin \pi q_\alpha \sin \pi q_\beta \quad (7.20)$$

for $\alpha \neq \beta$

For Oxygen I-Oxygen I and Oxygen 2-Oxygen 2

$$R_{\alpha\alpha} = \frac{4}{3} (A_1 + 2B_1) + 2A_2 + B_2 \quad (7.21)$$

and the off-diagonal element $R_{\alpha\beta} = 0$.

For Uranium-Oxygen I we find

$$R_{\alpha\alpha} = \frac{4}{3} (A_1 + 2B_1) \left(\cos \frac{\pi q_\alpha}{2} \cos \frac{\pi q_\beta}{2} \cos \frac{\pi q_\gamma}{2} - i \sin \frac{\pi q_\alpha}{2} \sin \frac{\pi q_\beta}{2} \sin \frac{\pi q_\gamma}{2} \right) \quad (7.22)$$

for the diagonal components, and

$$R_{\alpha\beta} = \frac{4}{3} (A_1 - B_1) \left(\sin \frac{\pi q_\alpha}{2} \sin \frac{\pi q_\beta}{2} \cos \frac{\pi q_\gamma}{2} - i \cos \frac{\pi q_\alpha}{2} \cos \frac{\pi q_\beta}{2} \sin \frac{\pi q_\gamma}{2} \right) \quad (7.23)$$

for the off-diagonal components.

For Uranium-Oxygen II

$$R_{\alpha\alpha} = -\frac{4}{3} (A_1 + 2B_1) \left(\cos \frac{\pi q_\alpha}{2} \cos \frac{\pi q_\beta}{2} \cos \frac{\pi q_\gamma}{2} + i \sin \frac{\pi q_\alpha}{2} \sin \frac{\pi q_\beta}{2} \sin \frac{\pi q_\gamma}{2} \right) \quad (7.24)$$

for the diagonal elements, and

$$R_{\alpha\beta} = \frac{4}{3} (A_1 - B_1) \left(\sin \frac{\pi q_\alpha}{2} \sin \frac{\pi q_\beta}{2} \cos \frac{\pi q_\gamma}{2} + i \cos \frac{\pi q_\alpha}{2} \cos \frac{\pi q_\beta}{2} \sin \frac{\pi q_\gamma}{2} \right) \quad (7.25)$$

for the off-diagonal components.

For Oxygen 1-Oxygen 2 we find

$$R_{\alpha\alpha} = -2A_2 \cos \pi q_\alpha - 2B_2 (\cos \pi q_\beta + \cos \pi q_\gamma) \quad (7.26)$$

with the off-diagonal elements vanishing.

The wave-vector $\vec{q}$ here is expressed as

$$\vec{q} = \frac{2\pi}{a} (\hat{q}_1 \hat{i} + q_2 \hat{j} + q_3 \hat{k}). \quad (7.27)$$

We also note here that there are some differences in the above expression from those occurring in the paper by Dolling, et al.,⁽⁶⁶⁾ but since the above expressions satisfy infinitesimal translation invariance, we believe that they are the correct ones - infinitesimal translation invariance manifests itself in the expression

$$\sum_{K'} R_{\alpha\alpha}^{(q=0)}{}_{KK'} = 0. \quad (7.28)$$

The parameters A_1 , B_1 , etc. are given, as stated, by fitting the calculation to the measured dispersion curves. The model is now completed by including the pure Coulomb interactions between the shells and cores of the atoms. The expressions for the Coulomb matrix elements are given in the appendix in the first principle computations and will not be repeated here. The numerical work now necessary to calculate the scattering kernel for UO_2 is in progress and will hopefully be completed in about two months.

8. SPECTRAL STUDIES IN A U^{238} SPHERE

A 20-in. diameter sphere of depleted uranium (0.22% U^{235}) was fabricated by Union Carbide for spectral studies at the General Atomic LINAC. The purpose of these studies was to provide spectral data that could be used to check fast reactor design computing methods and U^{238} cross section sets. The uranium sphere was cast in such a way that a target could be located at its center and neutron beams could be extracted from various holes of 1.185 in. diameter at different depths perpendicular to the source - LINAC axis. The hole pattern illustrated in Fig. 8.1 permitted measurements to be made at various angles to five radius vectors. The sphere was mounted on bearings and placed on a fully adjustable table to permit easy alignment to the flight path center line. Figure 8.2 shows a photograph of the uranium assembly in the measurement position (the collimator is outside the picture to the left). The target was a 3-in. diameter depleted uranium ball inside a stainless steel shell designed for water cooling. This target produces neutrons with reasonably good isotropy.⁽⁷⁷⁾ Preliminary calculations with cross sections for U^{238} which were evaluated by Joanou and Stevens⁽⁷⁸⁾ and the 1DF transport theory code⁽⁵³⁾ indicated that the target cooling water contributed substantial numbers of low energy neutrons to the spectrum at all positions. This effect is shown in Fig. 8.3. It was thus evident that the presence of a water coolant would significantly affect the interpretation of the data to be measured; therefore air cooling was used for the spectral studies.

Spectrum measurements were made at various positions in the sphere by the time-of-flight method using a 50-meter flight path. A 5-in. diam. NE-213 detector (proton recoil), described in Ref. 79, was employed

Fig. 8.1--Geometry of the 20 in. diam depleted uranium sphere

Fig. 8.2--Photograph of the 20 in. diam uranium sphere in the experimental room

Fig. 8.3--Calculated effect of target water coolant on the U^{238} sphere spectra

for the neutron energy range $E > 400$ KeV and a 5-in. diam. NE-908 (lithium glass detector), described in Section 11.3, was used for the energy range $E < 1.5$ MeV. The measurement position was obtained by removing the appropriate uranium insert plugs, all other holes being filled. The neutron source intensity was monitored by means of a 1/4-in. diam. U^{235} fission monitor placed in an auxiliary hole in the sphere and by a 1-in. diam. U^{235} fission room return monitor located in a corner of the experimental room. Also used were 1-in. diam. 5-mil thick gold foils located at positions E and L (Fig. 8.1) and a 5-mil 1 in. x 0.25 in. gold strip placed in an auxiliary hole in the sphere near the source. The gold foils appeared to provide the most accurate monitoring of the neutron source.

Comparative calculations of the spectra have been made and reported previously.⁽⁵⁸⁾ These calculations used a spectrum measured by Gayther and Goode⁽⁸⁰⁾ to describe the isotropic source at the center of the U^{238} target. Figure 8.4 shows this distribution. This spectrum was used because the one measured at General Atomic from the water-cooled target was considered inappropriate and no measurement of the air-cooled target spectrum had been made at that time. This measurement has since been done using the same flight path and detectors employed with the U^{238} sphere. The new target spectrum is depicted in Fig. 8.5 and shows some significant differences with the data of Gayther and Goode.⁽⁸⁰⁾ These include the different temperature of the Maxwellian fit to the curve (540 KeV instead of 300 KeV) and the surplus of neutrons outside this distribution above 1.5 MeV. This measured target spectrum has therefore been used in comparative calculations performed at the end of this quarter. These calculations supersede the comparisons reported previously⁽⁵⁸⁾ in which apparent differences of some magnitude were observed between theory and experiment.

The calculations were performed using the 1DF transport theory code⁽⁵³⁾ with S_{32} Legendre-Gauss quadrature. The high order quadrature was considered necessary to describe the rapid variation of the angular

flux which is very highly peaked in the outgoing ($\mu = 1$) direction. The angles and weights for positive μ are given in Table 8.1; these are symmetric about $\mu = 0$. The broad energy group structure is listed in Table 8.2. Two cross section sets were used, one due to Joanou and Stevens,⁽⁷⁸⁾ the other being the ENDF/B set.⁽⁸¹⁾ The source was treated as being isotropic and uniform in a 1.6 cm diam sphere at the center of the target. Table 8.3 lists the radius and angle of the experimental positions and the corresponding position used for the computation.

The comparison of measurement and theory for all positions has not yet been completed, only two positions are reported here. Figures 8.6 and 8.7 compare theory and measurement at positions C and M respectively. In these comparisons, no account has yet been taken of intensity variation from the one position to the other. Position C theory is in fact low, a result believed to be due to the fact that the true source is somewhat more widely distributed in space than is allowed for by the present calculation. In general, the agreement between experiment and theory is quite good over the energy range 5 keV to 12 MeV when ENDF/B cross section are used. The agreement is less satisfactory when the Joanou and Stevens cross sections are used. It is of great importance that these preliminary comparisons show that the theoretical spectra are quite sensitive to the choice of cross section sets and that the experimental data are of sufficient quality to specify which choice should be made. It is interesting to note that the shape of the theoretical spectra at Positions C and M is identical below 40 keV. This is the region dominated by elastic scattering, since the first excited level in U^{238} is at 45 keV and the next at 148 keV. On the other hand, the shape of the experimental spectra at Positions C and M appear to be the same up to 200 keV. This difference is presently not understood. Preliminary results indicate that this difference exists at other positions as well. For this reason, it appears that the spatial depletion of the higher energy flux will be a better test of the U^{238} inelastic scattering cross sections than will be the growth of the neutron flux below 40 keV.

Fig. 8.4--Source spectrum for a U^{238} target due to Gayther and Goode

Fig. 8.5--Leakage flux spectrum from the air cooled uranium target

Table 8.1
 LEGENDRE-GAUSS POSITIVE
 DIRECTION COSINES AND
 WEIGHTS FOR S_{32} COMPUTATIONS

<u>Direction Cosine</u>	<u>Weight</u>
0.9973	0.00351
0.9856	0.00814
0.9648	0.01270
0.9349	0.01714
0.8963	0.02142
0.8494	0.02550
0.7945	0.02934
0.7322	0.03291
0.6630	0.03617
0.5877	0.03910
0.5009	0.04166
0.4214	0.04383
0.3319	0.04559
0.2393	0.04692
0.1445	0.04782
0.0483	0.04827

Experimentally the data are very satisfying because the energy resolution is good, the overlap of the two detector systems is very reasonable, and the energy range studied is most pertinent. Nevertheless, some minor changes in these data may be expected when the improved lithium glass detector efficiency becomes available and when the target source description is refined. The comparison of theory and experiment including ratios at all the measured positions will be reported at the end of the next quarter.

Table 8.2

ENERGY GROUP STRUCTURE FOR U^{238} SPHERE COMPUTATION

<u>Group No.</u>	<u>Energy Range</u>	<u>Lethargy Width</u>
1	14.92 - 6.703 MeV	0.8
2	6.703 - 4.493	0.4
3	4.493 - 3.012	0.4
4	3.012 - 2.019	0.4
5	2.019 - 1.353	0.4
6	1.353 - 0.821 MeV	0.5
7	821 - 497.9 keV	0.5
8	497.9 - 302	0.5
9	302 - 183.2	0.5
10	183.2 - 111.1	0.5
11	111.1 - 67.38	0.5
12	67.38 - 40.87	0.5
13	40.87 - 24.79	0.5
14	24.79 - 15.03	0.5
15	15.03 - 9.119	0.5
16	9.119 - 5.531	0.5
17	5.531 - 2.035	1.0
18	2.035 - 748.5 keV	1.0
19	748.5 - 101.3 eV	2.0
20	101.3 - 1.855 eV	4.0

Table 8.3

EXPERIMENTAL AND COMPARATIVE CALCULATIONAL POSITIONS
AND ANGLES IN U²³⁸ SPHERE STUDIES

Position	Radius (cm)	Experimental Direction Cosine	Corresponding Calculational Direction Cosine(s)
A	10.79	1.0000	0.9973
B	16.51	1.0000	0.9973
G	22.25	1.0000	0.9973
C	10.79	0.9514	0.9349) Average 0.9648)
D	16.51	0.9783	0.9856
H	22.25	0.9879	0.9856
J	10.79	0.7650	0.7322) Average 0.7945)
E	10.79	-0.7650	-0.7322) Average -0.7945)
F	16.51	0.8760	0.8494) Average 0.8963)
L	16.51	0.7463	0.7322
K	16.51	-0.7463	-0.7322
M	22.25	0.8336	0.8494

Fig. 8.6--Comparison of measured and calculated neutron spectra at position C in the U^{238} sphere

Fig. 8.7--Comparison of measured and calculated neutron spectra at position M in the U^{238} sphere

9. KINETIC STUDIES IN U-238

9.1 INTRODUCTION

The experimental kinetic studies which are reported here consist of space dependent neutron dieaway studies in a fast, very slightly multiplying assembly made of highly depleted uranium. These studies have included different detectors of various energy responses, in order to obtain some information on time, energy, and space coupling. The results are based on several experimental runs conducted during the past year. Several plausible explanations for some of the observed phenomena are given in the description of the results. However, an extensive theoretical analysis, as outlined in Section 9.3, will be conducted in the forthcoming year.

There are three basic motivations for conducting such measurements. First the kinetic studies emphasize aspects of neutron interactions somewhat differently from the steady state spectra. Thus, they provide additional integral checks on the theory, computational methods, and cross section data. For fast multiplying systems, which are not very far from critical (e.g. $k_{\text{eff}} > 0.8$), and where hopefully a well-isolated persisting eigenvalue exists, the kinetic studies should supply the same excellent integral check of the system under study as for thermal systems.

The second motivation is to develop the experimental capability of measuring accurately extremely fast transients in the presence of high gamma fields (typical to power reactors) which decay rapidly (typical to linear accelerators).

The third purpose of the present set of measurements was to obtain adequate information on the mean emission times and their variance at the

same locations where the time-of-flight steady state spectra were measured.

9.2 GEOMETRY

The measurements were made in the 20-in. diam. depleted uranium sphere described in Section 8. These dieaway measurements utilized the same geometry employed for the spectral studies. The reentrant holes (see Fig. 8.1) for the spectrum measurements were used for insertion of the detectors for the kinetic studies. Since the detectors inserted into the sphere essentially responded to the scalar flux, measurements at various angles yielded important information on the perturbation introduced by the detector itself and by the removal of the uranium plugs.

The uranium sphere was positioned in the middle of a shielded room. The side walls of that room were far from the sphere, but the ceiling and the floor were at a distance of 1.5 m, which was expected to enhance the room return effect. This point was carefully scrutinized, as mentioned in the following sections.

9.3 DETECTOR

The detector used in these experiments was a solid state detector (S. S. D.) used with a neutron conversion foil. The conversion foils employed here were fission foils with different energy responses. The conversion foils used were primarily U^{238} , Np^{237} , and in one case U^{234} . (The two last foils are threshold foils). The particles detected by the S. S. D., namely fission fragments, produce a large charge pulse. This fact and the small volume of the detector make the latter extremely useful in the presence of the high transient gamma field which is encountered when using a LINAC.

The solid state detector used a silicon wafer which was fully depleted (diffused junction type). The dead-window thickness as quoted by the manufacturer was less than 1 micron, and the total thickness was 100 microns. The effective diameter of the detector was 0.44 in. (100 mm²

effective area). The use of a fully depleted silicon S.S.D. is to be recommended when LINAC sources are used because the charge collection time is extremely short (a few nsec at most) for the entire detector and the recovery from the gamma flash is fast. If a partially depleted detector were used, a long tail would probably appear as a result of the gamma flash, due to the lack of electrical field in the undepleted part. Such a tail would cause a slow recovery from the flash, thus making it impossible to measure neutron fluxes at very early times following the neutron burst.

9.4 ELECTRONICS

9.4.1 General

Stringent demands on the electronics (and detection system) are imposed by this type of kinetics study. They are: low noise, low rf pick-up, very fast response, very fast recovery from the gamma flash overload, reasonable linearity, and relatively high amplification. It is obvious that these demands are not complementary. However, the use of a solid state detector with a fast current preamplifier, fast nanosecond logic units which are now commercially available, careful rf shielding and impedance matching provided a satisfactory counting channel. The block diagram of the final counting channel used in most of the runs reported here is given in Fig. 9.1.

The basic function of the various units in the block diagram is explained below:

1. The S.S.D. with its conversion foil was rigidly attached to the fast current preamplifier ((2) in Fig. 9.1) by 40 inches of 50Ω air-line. The air-line was used instead of normal cable in order to avoid excessive amount of hydrogenous material.
2. The battery and the potentiometer which were attached to the fast preamplifier were used to cancel a dc level of -250 mV on which the output pulses were previously superimposed. They could also be used to compensate for any long-time dc

(1) TOTALLY DEPLETED Si SOLID STATE DETECTOR WITH FISSION CONVERSION FOIL	(8) GATE AND DELAY GENERATOR (EG&G GG200)
(2) FAST CURRENT PRE-AMPLIFIER (SSR-112)	(9) TIME TO AMPLITUDE CONVERTER (EG&G TH200A)
(3) POWER SUPPLY FOR PRE-AMPLIFIER AND DETECTOR BIAS	(10) LOW NOISE LINEAR AMPLIFIER (ORTEC-410)
(4) DELAY BOX AND PULSE SHAPER	(11) MULTICHANNEL PULSE HEIGHT ANALYZER (TMC-210)
(5) FAST TRIGGER DISCRIMINATOR (EG&G T100A)	(12) AMPLIFIER
(6) FAST DC COUPLED LINEAR GATE (EG&G LG 101)	(13) DUAL SCALER
	(14) COUNT RATE METER

Fig. 9.1--Electronic block diagram for the kinetic studies

level associated with gamma-flash. The compensating voltage enabled the use of a fully dc coupled counting system, which was able to handle a very high count-rate ($\sim 10^8$ cps) without problems from pile-up or dc shifts.

3. The Linear Gate (6) was used, if necessary, to gate out the signal at very early times after the burst. The pulses at very early time may be due in part to the gamma-flash, or they can be neutron pulses superimposed on the decaying gamma-flash pulse. Whenever the gamma-flash is substantial, the proper gating time is of prime importance.
4. The function of the triggers (5) and (7) was to standardize the pulses. The first trigger was also used as a fast discriminator in order to discriminate against noise and small pulses riding over the tail of the gamma-flash. The proper discrimination of biasing was made by using temporarily a linear stretcher system, as described later.
5. The gate length for the linear gate was determined by the gate-generator, which was triggered by the accelerator injector pulse. This pulse preceded the actual gamma-flash by about 2.8 μ sec.
6. Two time analyzers were simultaneously used in parallel during these experiments. For "coarse" time channels ($\Delta t \geq 31.166$ nsec) which cover the long time span, a TMC 201 (and sometimes TMC 211) time-of-flight multichannel analyzer was used. For the decay at early times after the burst, an external time-to-amplitude converter (TAC) was used, as described in Fig. 9.1. The output pulses from the TAC, which are essentially proportional to the time interval between the burst and the moment of the detection of the neutron, are amplified by a

linear amplifier (10) to take advantage of the full range of the multichannel pulse height analyzer (11).

9.4.2 Discrimination Procedure

Though the fast pre-amplifier is reasonably linear, no multichannel analyzer is fast enough to process the pulses and deliver a representative pulse height spectrum. This spectrum is important for proper biasing of the discriminator. To adapt the linear fast pulses to the multichannel input, a pulse stretching process must be used. The stretching process used here involved a low noise amplifier which furnished a stretched pulse whose amplitude was proportional to the area under the fast linear pulses from the pre-amplifier. The stretching was done after applying the gate, so that unwanted pulses, e.g., gamma-flash, were gated out. In order to properly bias the signal, the multichannel pulse height analyzer accepted the stretched linear signal in coincidence with a pulse from the fast discriminator. The block diagram of a typical stretching system is shown in Fig. 9.2. The unbiased and biased energy spectrum of alpha particles from our Np^{237} conversion foil, as measured by this stretching system, is shown in Fig. 9.3. Most of this alpha activity is due to traces of the highly radioactive Pu-238. The relatively poor energy resolution, which is entirely adequate for kinetic studies, is due partly to the fast pre-amplifier, but is due mainly to the thickness of the alpha-source ($\sim 600 \mu\text{g}/\text{cm}^2$).

The discrimination level of the trigger-discriminator was determined at the beginning of the measurements and was checked occasionally during the run, through the above-mentioned linear channel. In the presence of a strong gamma-flash, there is a strong coupling between the discrimination level and the choice of the gate opening time (the delay).⁽⁸²⁾ The proper choice of this delay could be determined by checking the pulse height spectrum as a function of the delay.

Fig. 9.2--Electronic block diagram of the Linear Channel "Stretcher" used to check the discriminator in the fast kinetic studies

Fig. 9.3 --Alpha spectrum from the Pu^{238} contaminated Np^{237} foil

9.4.3 Calibration of the Time-to-Amplitude Converter (TAC)

Most of the measurements with the TAC were done with a time channel width of 1.024 nsec. A conservative estimate of the differential uncertainty in this width due to nonlinearity of the calibrating device, of the TAC, and of the pulse height analyzer is about 0.5%. This conclusion is based on several calibration runs and linearity checks. For the calibration run, a digital delay generator was used, which furnishes standard pulses within precisely pre-set delays. The first pulse was used to start the TAC and the delayed pulse to stop it. The number of channels within the pre-set delay time gave the average channel width in that time region. By varying the delay the whole range of the TAC was scanned. In our calibration run 100-nsec intervals were used. The results are shown in Fig. 9.4 for the 1- μ sec and 10- μ sec scales of the TAC.

A linearity check was conducted to investigate the channel-by-channel variation. Here random "stop" pulses were used which had no correlation to the "start" pulses. Thus a linear system at a relatively low count rate should have given a constant count per channel. The random source used was the alpha activity of the thick Np^{237} (and Pu^{238}) foil (at about 1500 cts/sec). The "start" pulse was furnished by a pulse generator and the stop pulse by an alpha pulse from the same setup used in the regular runs. The results are also shown in Fig. 9.4 for the 1- μ sec and 10- μ sec scales of the TAC. Except for nonlinearity during the first 100 channels, which is probably associated with the low level nonlinearity of the multichannel analyzer (TMC-210) and the TAC itself, the corrected response is constant. The correction mentioned here is for the shadowing effect which is described in Section 9.5A. During all dieaway runs, there was a constant delay so that the first 100 to 200 channels were never used. A similar calibration and linearity check was conducted on the TMC-201 time-of-flight unit with its 31.166 nsec per channel. The response was very flat and the channel width was found to correspond to the stated value within 0.1%.

Fig. 9.4--Calibration and linearity checks of the TAC

9.5 EXPERIMENTAL PROCEDURE

The actual experimental procedure was as follows. After positioning the detector at the desired location inside the U^{238} sphere, the proper functioning of most of the system was checked by looking for residual pulses due to the alpha activity of the fission foil. These pulses were biased out during the actual run.

The timing sequence starts by an injector pulse from the accelerator, triggering the gate-generator, which in turn closes the linear-gate for a prescribed time. This time had to be determined for each position since the amount of the gamma flash is considerably reduced when the source-detector separation is increased, due to the strong gamma attenuation by the uranium. The gate was usually on for almost all the time span covered by the widest multichannel time analyzer. The time response following the neutron burst was measured simultaneously by narrow and wide time channels. When the gamma flash was large enough, the zero time was determined by a short run with ungated systems. No constant background was detected in any of the runs. This was determined by reducing the electron current of the LINAC to zero, without changing any other parameters, such as the rf power which causes most of the noise pickup.

During all the runs the rf pulse of the LINAC was 1.6 μ sec, the electron (and the gamma) burst widths were either 7 or ~ 5 nsec. The repetition rate was normally 720 pps. The average electron current at the energy of 28 MeV was between 10^{-8} amp to 5×10^{-7} amp, depending on the source-detector separation. The equivalent peak intensity of neutrons was roughly 10^{13} to 10^{15} neutrons/sec.

9.6 RESULTS

9.6.1 Data Reduction

The raw experimental data are the recorded number of counts accumulated in the various time channels after a certain number of source

bursts. These basic data are first corrected for the shadowing effect, which is due to the basic logic of the time analyzer, namely its ability to accept only one "stop" pulse for each "start". Thus, the time channels following a busy channel, in which a "stop" pulse has been received, are unable to record any event during that cycle, hence they are shadowed. If C'_i is the total count accumulated in the i -th channel after M bursts, the corrected (for shadowing) total count in that channel is:

$$C_i = M \ln \left[1 - \frac{C'_i}{M - \sum_{j=1}^{i-1} C'_j} \right] \quad (9.1)$$

If the second term in the brackets is small compared to unity, then:

$$C_i = \frac{M}{M - \sum_{j=1}^{i-1} C'_j} C'_i \quad (9.2)$$

C_i reduces to C'_i when the number of bursts is much larger than the total count accumulated in all channels preceding channel i .

In applying Eqs. 9.1 and 9.2 to a set of data one has assumed a constant source intensity during the whole run. If the source intensity fluctuates appreciably, one has to apply an additional correction for the deviation of the source from its average value. The basic correction, Eq. 9.1, and the correction for significant intensity fluctuations are reliable (and small) for $M \gg \sum C_j$. In all the measurements reported here, the condition

$$\sum C_j / M \leq 0.16 \quad (9.3)$$

was fulfilled.

In principle one should also consider the count loss due to occurrence of two events within one channel. This is easily shown to be rather small, since

$$R \cong R' \left[1 - \frac{1}{2} \frac{C_i}{M} + \frac{1}{3} \left(\frac{C_i}{M} \right)^2 \dots \right] \quad (9.4)$$

where $R' = C_i / M \Delta t$ and R is the count-rate corrected for the above-mentioned count loss. As C_i is usually much smaller than M , it is evident that $R \cong R'$.

After correcting for the shadowing effect, the background (if nonzero) is subtracted. In a very few cases the data were also corrected to remove some small irregularities due to gamma flash residues in the first 30 to 40 nsec. However, in the great majority of cases, the gamma flash was suppressed by proper shielding and by electronic means and had hardly any effect on the results.

A convenient way for comparing results from different runs is to compare the corresponding instantaneous decay constant, $\alpha(t)$, or the logarithmic derivative. This quantity is independent of the source intensity and its constancy over a certain time interval may indicate the existence of a fundamental or pseudofundamental mode. However, since $\alpha(t)$ is related to the derivative of the decay curve, very high statistical precision is needed in the data in order to obtain reasonable precision in $\alpha(t)$. A least squares fit to a single exponential function over a small number of channels was the method used to calculate $\alpha(t)$. The calculated $\alpha(t)$ is then assigned to the mid-channel. The least squares fit program also furnished the statistical uncertainties associated with α .

9.6.2 Sensitivity to Electronics Details

In order to show the sensitivity of the experimental results to the electronic details data are reported for two runs made in the same location, $R = 11.8$ cm, using essentially the same electronic system except

for the gate. The results are shown in Fig. 9.5 where the logarithmic derivative $\alpha(t)$ is plotted as a function of time. The apparent rise in $\alpha(t)$ measured by the "old" system is due to the relative slow rise time, T_r , of the gating pulse used in this system. Using a faster gate with $T_r \sim 3$ nsec reveals the true behavior of $\alpha(t)$ at early times, namely a rapid decrease. It should be noted that beyond 200 nsec the two runs coincide rather well.

9.6.3 Effect of Room Return

It is usually very difficult to eliminate the effect of room return neutrons in a small fast system. It is therefore of prime importance to determine the magnitude of their effect. Three separate measurements showed that the effect of room-return in our experimental arrangement was quite small.

The first measurement that could indicate the existence of a room-return effect was the dieaway measurement in an open channel at a radius of 20.32 cm (Position 2 see Fig. 8.1). In this open channel, both sides of the detector were completely exposed to the room. The first observed integral effect was the background level, that is, the average count rate at long times after the burst ($t \geq 120 \mu\text{sec}$). The background at this position, in the open channel, amounts to about 12.5 c/sec, while at $R = 9.8$ cm (Position 2, Fig. 8.1) it amounted to 2.5 c/sec. This is in contrast to the fact that the time integrated flux in Position 1 was much higher than in Position 2. This effect on the background indicates, from flight time consideration, that the contribution of the room return in the considered time domain is mainly due to direct exposure of the detector in the open channel to low energy neutrons, $E < 100$ eV.

The effect of fast neutrons returning from a nearby concrete and lead wall and detected by the exposed detector in Position 2 is shown in Fig. 9.5(b). The function $\alpha(t)$ measured at this position shows a sudden change in the slope of the decay curve at 250 to 300 nsec after the burst.

Fig. 9.5--Instantaneous decay constants at (a) $R = 11.8 \text{ cms}$ and
(b) $R = 20.23 \text{ cms}$ in the uranium sphere

This time corresponds to the flight time of 1 MeV neutrons to the nearest wall and back. The fact that this phenomenon is missing in the other measurements supports the assumption that it is due to room return. Except for the room return effect, the $\alpha(t)$ curve at Position 2 follows the same pattern as in all other measured positions. Another test was performed which was intended to assess the effect of an enhanced room return on the actual measurement. This was done by measuring the dieaway at two locations with and without the presence of a nearby stack of concrete. A 4 ft by 3.5 ft by 3 ft stack of concrete bricks was placed at a distance of 3.5 ft (108 cm) from the sphere, on the side nearest to the detector. The decay curves were measured at a distance of 13.1 cm (Position E') and 7.6 cm (Position F'), see Fig. 8.1) from the surface of the sphere. Comparison of the decay curves, channel by channel shows that the behavior at these positions, with and without the concrete, is identical within two standard deviations (2σ). Furthermore, the deviations larger than one standard deviation do not show any systematic pattern. As an example, the ratio of the count in corresponding channels accumulated at Position F' with and without the concrete is shown in Table 9.1. The channel width was 31.166 nsec.

Another fact which supported the belief that room return had negligible effect was the observation that the neutron background at the two measured positions was the same both with and without the concrete stack. The background, which was very low, was defined in this case as the average neutron population from about 7.5 μ sec to 30 μ sec after the gamma flash.

A third measurement which added support to the above conclusions was the great similarity of the time behavior of the decaying flux near the surface, namely Position H which is 2.25 cm from the surface, to the flux measured at interior positions. This is illustrated by the flux ratios shown in Fig. 9.6.

Fig. 9.6--Spatial dependence of the time behavior of the neutron flux in the U^{238} sphere (U^{235} conversion foil)

Table 9.1

RATIO OF THE DECAY CURVES AT POSITION F'
WITH AND WITHOUT THE NEAR-BY CONCRETE PILE

<u>Channel No.</u>										
1	2	3	4	5	6	7	8	9	10	11
<u>Ratio</u>										
1.12	1.23	1.21	1.19	1.20	1.22	1.20	1.24	1.20	1.25	1.24
<u>Channel No.</u>										
12	13	14	15	16	17	18	19	20	21	22
<u>Ratio</u>										
1.19	1.19	1.18	1.23	1.22	1.18	1.23	1.22	1.18	1.18	1.22
<u>Channel No.</u>										
23	24	25	26	27						
<u>Ratio</u>										
1.15	1.31	1.32	1.25	1.2						
<u>Channel No.</u>										
28-32	33-37	38-43	44-56							
<u>Ratio</u>										
1.22	1.13	1.16	1.23							

9.6.4 Effect of Perturbation

Several dieaway measurements were made at positions having about the same radius, but in holes with different angles to the radius-vector, which could be obtained by placing the detector at various reentrant holes in the sphere. Since one actually measured the scalar flux, these measurements yielded information on the perturbation introduced by the detector and by the removal of the uranium plugs. Comparison of the decaying curves and the instantaneous decay constants did not show any noticeable effect due to the above-mentioned perturbation. For example, the normalized ratios of the decay curves at Position D' ($R = 17.37$ $\Theta = 26^\circ$) and Position F' ($R = 17.8$ $\Theta = 44^\circ$), shown in Fig. 9.6(b), are rather similar.

In addition these curves are rather close in shape to those shown in Fig. 9.6a which are measured at positions E($R = 12.3$ cm, $\Theta = 61^\circ$) and H(23.1 cm, $\Theta = 24^\circ$).

9.6.5 Neutron Decay at Long Time

The high neutron intensity delivered by the linear accelerator enables one to measure the neutron decay over a wide span of time. The results of two such measurements are shown in Figs. 9.7 and 9.8. Fig. 9.7 covers the time span from about 100 nsec to about 100 μ sec. The first few microseconds were measured with 31.66 nsec (per channel) time resolution and the remainder of the interval was measured with 250 nsec per channel. In Fig. 9.8a, the decay at Position D' ($R = 17.37$) from about 30 nsec to 6 μ sec is shown. The instantaneous decay constant, $\alpha(t)$, associated with this decay is shown in Fig. 9.8b. The $\alpha(t)$, was obtained, as explained in Section 9.6.1, by a least squares fit over four successive channels. The first channel in the fit is then advanced by one for the determination of $\alpha(t)$ in the next interval, and so forth.

A measured curve $\alpha(t)$ covering a rather large time span with a reasonable precision is shown in Fig. 9.5a. In the same figure the results of least squares fit over 750 nsec to a single exponential are also plotted. They show the inadequacy of forcing the fit of a single exponential to a nonexponential function.

The decay curves and the plots, $\alpha(t)$, clearly show the absence of a single exponential decay. Instead, one obtains a continuously decreasing decay constant as a function of time. The decrease in $\alpha(t)$ is rather slow, except for early times, and in fact it becomes even slower as time progresses.

The measurements disagree with an earlier observation⁽⁸³⁾ of a single decay constant in a large depleted uranium system. The single decay constant measured⁽⁸³⁾ with a U^{235} fission chamber between 500 nsec and

Fig. 9.7--Wide range decay of the neutron population
 in the depleted uranium sphere

Fig. 9.8--Decay curve (a) and instantaneous decay constants (b) measured by U^{235} conversion foil at $R = 17.37 \text{ cms.}$ (Position D')

1500 nsec is $(3.52 \pm 0.17) \times 10^6 \text{ sec}^{-1}$. The instantaneous decay constants measured with the U^{235} conversion foil in two locations in the 20-in. sphere in a similar time range are given in Table 9.2. Although one obtains similar decay constants to those reported in this range, the statistical significance is rather low.

Table 9.2

INSTANTANEOUS DECAY CONSTANT AS FUNCTION OF TIME

<u>Position</u>		<u>R = 11.7 cm</u>	
<u>Time Interval</u> <u>(nsec)</u>	<u>$\alpha(t)$</u>	<u>$\times 10^6$</u>	<u>$\pm \Delta\alpha$</u>
410 - 1410	3.51		0.95
440 - 1440	3.35		0.91
470 - 1470	3.19		0.85
505 - 1505	3.04		0.80
535 - 1535	2.91		0.78
565 - 1565	2.81		0.78
<u>Position</u>		<u>R = 17.37</u>	
50 - 800	8.29		0.90
300 - 1050	3.83		0.30
550 - 1300	2.90		0.20

The curves shown in Figs. 9.5 and 9.6 indicate a relatively weak space-time dependence of the energy integrated fission rate of U^{235} , for times longer than a few hundred nanoseconds. This result is to be expected in a material of high mass number whose elastic scattering is large compared to the nonelastic scattering, a situation which is valid in U^{238} below about 0.8 MeV. Such a system can be fairly well approximated by age theory, in which the energy of the neutron and the time from birth are uniquely related.

The plausible physical explanation for this behavior is the fact that the source neutrons had to make a substantial number of elastic collisions and hence have diffused away from the source. The neutron population in the various locations inside the sphere, excluding its boundaries,* is then more characteristic of the sphere as a whole than of the spectrum of the source. However, it should be clear that the apparent separability of space and time (and energy) in the uranium sphere, which was also observed in other materials,^(84, 85) is by no means exact. No mathematical separability is obtained even in the age-theory. Thus, the application of a geometrical buckling to eliminate the space variable⁽⁸⁵⁾ must be substantiated by careful experimental proof for the practical applicability of this quantity.

The fact that the decay is by no means asymptotic is clearly shown in Figs. 9.5 and 9.8 by the continuous variation of the instantaneous decay constant $\alpha(t)$. The apparent approximate separability of space and time at long times is also a strong argument against interpreting the observed data in terms of the presence of long-living high order spatial harmonics.

9.7 NEUTRON DECAY AT EARLY TIMES

a. Measurements With U^{235} Conversion Foil

The neutron decay at long times in various positions did not show a strong space dependence, as is evident, for example, from Figs. 9.6a and 9.6b. However, the same figures show a somewhat stronger position dependence at early times. To investigate this point more carefully the neutron population decay at early times was measured with about a 1-nsec time resolution. The decay curves from time zero to 300 nsec measured at two positions: pos 1 ($R = 9.8$ cm) and pos F'

*The leakage from the 20-in. uranium sphere is not high. The diffusion leakage at 1 MeV amounts to about 2 percent.

($R = 17.8$ cm) with U^{235} conversion foil are shown in Fig. 9.9. Position 1 was the closest position to the center (and thus to the bremsstrahlung source) which furnished reliable results, without excessive gamma flash pulses. In this position one sees the buildup of neutrons during the gamma flash, which was ~ 7 nsec wide. This buildup consists mainly of uncollided source neutrons since the effective full width at half maximum around the peak is approximately 10 nsec, which is close to the actual width of the gamma burst. The immediate decay (see Fig. 9.10) following the pulse has a decay constant of about 5×10^{-7} sec $^{-1}$, which is believed to characterize the removal of neutrons around the maximum of the spectrum, namely 0.5 to 1 MeV, mainly by inelastic collisions. The subsequent decay gradually approaches, after approximately 250 nsec, the decay curves obtained at other locations.

As one goes farther from the neutron source the amount of uncollided neutrons measured by the U^{235} foil rapidly diminishes. At a radius of 11.7 cm (Position C, not shown in Fig. 9.9), the uncollided flux is already overshadowed by the collided flux which extends over a large energy range and hence, also a large time interval. Since the fission cross section of U^{235} rises slowly with decreasing energy, all energies contribute to the decay curve and rapidly smear the pulse of uncollided flux.

Another effect which is associated with the former one, is a shift of the time at which the population peak is achieved. This can be interpreted as fast neutron wave propagation in the sphere. (84)

Fig. 9.9--Decaying neutron flux measured at Positions 1 and F'

Fig. 9.10--Instantaneous decay constants measured at Positions 1, C' and F'

b. Measurements With Np^{237} and U^{234} Conversion Foils

To obtain some information on the high-energy-time coupling, threshold conversion foils were used instead of the U^{235} fission foil. In the first runs a U^{234} fission threshold foil (thick coating of U^{234} sulfate on platinum)* was used. The instantaneous decay constants measured with this foil and with U^{235} at $R = 11.4$ cm are shown in Fig. 9.11. The interval least squares fit for $\alpha(t)$ was three channels, the channel width being 31.166 nsec. The initial decay as measured by the U^{234} foil seems to be somewhat faster. The subsequent decay obtained by means of the U^{234} coincides with that of the U^{235} probably due to the presence of 17% of U^{235} in the U^{234} foil. The Np^{237} foils used later on were much purer (there were only minor traces of Pu^{238}). The threshold energy is about the same as for U^{234} , namely ~ 0.7 MeV. The decay curve observed by the Np^{237} fission foil shown for comparison in Fig. 9.9 is much steeper than the characteristic decay curve measured by the U^{235} foil at the same location. This is to be expected since the former measures neutrons above 0.7 MeV, while the latter has a wider energy response. Degradation to lower energies below the inelastic threshold reduces the effective removal rate $\langle \sigma \Sigma \rangle_{\text{eff}}$, and hence the U^{235} detector observes a slower decay.

The decay curves measured by the Np^{237} detector at two positions $R = 11.7$ and 17.8 cm are quite different, as shown in Fig. 9.12. The decay is faster at the location which is closer to the source (Pos. C'). Naturally, in this position the buildup of the neutron population is also faster.

*The U^{234} and Np^{237} were prepared by G. Main of ANL.

Fig. 9.11--Instantaneous decay constants measured at $R=11.4$ cm

Fig. 9.12--Decaying neutron flux measured by the Np^{237} conversion foil at Positions C' and D'

The interesting feature of the neutron decay as measured by the Np^{237} detector is its apparent exponential behavior over a relatively large portion of the decay. In position R = 11.7 cm it extends from about 30 nsec to 80 nsec which covers two and a half-decades of decay. In the position farther from the source, R = 17.8 cm, it extends over the same time interval which covers one and a half decade of decay. This apparent exponential feature appears more obvious in Fig. 9.13 where $\alpha(t)$ is plotted for the two above-mentioned positions. The least squares fit interval for $\alpha(t)$ was 40 channels (each 1.024 nsec in width) and the gap between successive fitting intervals was four channels.

The measured decay is by no means asymptotic, as is demonstrated by the fact that α is measured to be $(5.9 \pm 0.2) \times 10^7 \text{ sec}^{-1}$ at R = 11.7 and $(4.62 \pm 0.15) \times 10^7 \text{ sec}^{-1}$ at R = 17.8 cm.

The Np^{237} response at times longer than ~ 100 nsec is not exponential, at least not with the same statistical significance as for the early time decay. The decay at longer times is slower and is described by a monotonically declining decay constant as shown in Fig. 9.14.

It may be noted that a similar observation of a "semi-exponential" decay at early times can be stated with regard to the U^{235} detector. However, the time interval of its existence is shorter and the statistical significance somewhat smaller. At position C!, R = 11.7 cm, $\alpha(t)$ between $40 \leq t \leq 65$ nsec is equal to $(1.75 \pm 0.08) \times 10^7 \text{ sec}^{-1}$. At a position farther from the source, Pos. F!, between 50 to 90 nsec, α equals $(1.01 \pm 0.07) \times 10^7 \text{ sec}^{-1}$.

Fig. 9.13--Decay constants measured by the Np^{237} conversion foil at Positions C' and D'

Fig. 9.14--Decay constants at lag times measured by the Np^{237} conversion foil at Positions C' and F'

c. A Plausible Qualitative Explanation for the Early Time Behavior of the Neutron Population

It was suggested by Storrer and Stievenart⁽⁸⁶⁾ that a pseudo-fundamental mode might exist in a pure U^{238} medium for energies above the fission threshold of U^{238} , namely $E \sim 1.5$ MeV. We can investigate this point and other aspects of the early decay with the help of group cross sections obtained by the GAM-II code⁽⁸⁷⁾ for an infinite highly depleted U^{238} medium.

Using the appropriate average cross sections, one can calculate an infinite multiplication factor, k_{∞} which essentially describes the multiplication in Groups 1 to 6 (i.e., above 0.8 MeV).

The value obtained is 0.414. Since the sphere is quite large, one may use this value as an approximate prompt effective multiplication factor, k_{eff} . The value of the inverse lifetime for the first six energy groups is calculated to be approximately

$$\langle 1/\ell \rangle_{1-6} = 3.1 \times 10^8 \text{ sec}^{-1}$$

These two values yield the prompt fundamental decay constant, α , of the multiplying medium under consideration,

$$\alpha = \frac{k_{eff}^{-1}}{\ell} = -1.9 \times 10^8 \text{ sec}^{-1} \quad (9.5)$$

such a short decay period (~ 5 nsec) was not observed. This point could have been tested unambiguously by a U^{238} fission foil. However, the count rate obtained using this detector was prohibitively low.

The exponential decay of the Np^{237} detector may possibly be due to a "pseudotrapping" effect. In Fig. 9.15 it can be seen

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$\Sigma_{ne}(E) \text{ CM}^{-1}$

Fig. 9.15--Pertinent cross sections of U^{235} , U^{238} , and Np^{237}

that the threshold fission cross section of Np^{237} is rising rapidly in the region where the removal (mainly by inelastic scattering) cross section of the uranium, Σ_r , has considerably decreased. The neutrons in the energies above 0.8 MeV rapidly lose their energy due to the high inelastic scattering cross section. Below this energy the loss rate due to inelastic collision is much lower and hence the neutron population would be expected to build up. The remaining loss rate would then be governed by the much lower, almost constant, nonelastic cross section. The energy range from the threshold of the Np^{237} detector to the step-rise in the nonelastic cross section of the U^{238} is quite small, approximately 0.2 MeV. Thus, the Np^{237} detector may be measuring the decay of a "trapped-semimonoenergetic" neutron population, and this decay will be exponential since the loss rate is proportional to the instantaneous population. Though the decay is essentially exponential in the time interval considered, the decay constant is not independent of position since the energy spectrum is a function of position particularly at these early times. Similar results, but with poorer precision, were obtained with the U^{234} detector. This foil has a threshold close to that of Np^{237} .

Inelastic collisions with small energy loss and elastic collisions slowly change the one-group feature of the neutrons and probably cause the slower, nonexponential decay at later times ($t > 80$ nsec).

Using the removal group cross sections out of the "trapping-groups" ($0.2 \leq E \leq 1.4$ MeV), and a proper weight one obtains the following removal rate: $\langle V \Sigma_r \rangle_{6,7} = 4.7 \times 10^{-7} \text{ sec}^{-1}$. The infinite medium scalar group spectrum (from a GAM-II⁽⁸⁷⁾ calculation) was used to determine the relative contribution of Groups 6 and 7. This value for the removal rate is in fair

agreement with the decay constant obtained by the Np^{237} detector at Position F', namely at $R = 17.8$ cm. This radius is probably far enough from the source, so that the latter does not affect the decay rate.

The rapid energy loss of the neutrons above approximately 0.8 MeV due to inelastic collisions with the U^{238} atoms, means a rapid buildup of the neutron population below this energy. As one moves farther from the source, this buildup cannot be observed, since the collided softer spectrum prevails there. The neutrons are accumulated in the energy domain between 0.8 and 0.1 MeV since most of the inelastic scattering of source and fission neutrons leads them to this energy interval. The inelastic reaction rate in this region is smaller by about a factor of six and in addition, many inelastic collisions do not result in a large energy loss. Hence, the neutron accumulation in this limited energy interval will persist until the remaining nonelastic scattering and leakage deplete the neutron population and soften it. This physical picture might explain the observation that the U^{235} detector, which does not ignore neutrons of any energy, still reveals in a limited short time interval, a semi-exponential decay. This decay is still probably governed by the inelastic collision rate, however, averaged over a larger energy domain as compared to the threshold detector. In the case of the Np^{237} detector the lower energy boundary of the spectrum was determined by the detector efficiency, i.e., threshold fission cross section of the Np^{237} . The spectrum observed by the U^{235} detector is broader and thus the semi "mono-energetic" behavior is less obvious.

A quantitative proof for these explanations would necessitate an appropriate mathematical model to describe the inelastic

cross sections in the region of interest. It is quite conceivable that the basic methods and techniques which are used to explain the trapping effect for thermal neutrons in crystalline beryllium^(88, 89, 90) could apply with some modifications to the present problem.

9.8 NOTES ON THE THEORY

The lack of a distinct decay constant (persisting mode) is typical of the far subcritical state and nonmultiplying systems, and makes the comparison between theory and experiment difficult. The most straightforward way of doing such a comparison is to compute the full time and energy dependent response of a system to an instantaneous burst. This problem is, of course, not an eigenvalue problem but a source calculation covering a large span of time. It necessitates a good representation of the source in space and energy. Most of the codes which do this type of calculation are very complicated and were designed usually to perform safety analysis, - excursion calculations, or xenon oscillations. Therefore, they have provision for only a few energy groups and usually their results are not expected to be very precise. Nonetheless, the availability of such a diffusion code if generalized to include many energy groups, say 10 to 20 groups, would be helpful for qualitative comparison with the experiment. Naturally when diffusion theory is applicable the significance of the comparison is highly enhanced.

A general time-dependent one-dimensional diffusion theory code GAKIN⁽⁹¹⁾ has recently been developed at General Atomic and was successfully tested in a multi-zone system using two groups. It is hoped that this code can be extended usefully to as many as 20 energy groups and to very short times.

The actual comparison between the output of such codes and the experiment should be done in a consistent manner. If, for instance, the

quantity compared is the instantaneous period, $\alpha(t)$, i. e., the logarithmic derivative, the same averaging that is inherent in the experimental data, (e. g., an exponential fit over short time intervals) has to be applied to the theoretical time dependent flux. It should be noted, however, that to get statistically meaningful $\alpha(t)$, one needs a very high count rate over all the time range. While this is feasible at early times, it becomes almost impossible for later times. For example, in the U^{238} sphere the low count rate "region" begins at about 250 nsec after the burst. Under these circumstances another practical approach is to take any functional ratio of the decaying flux. A very simple ratio is of two integrals, one taken at early times and the other at later ones, similar to the shape methods.⁽⁹²⁾ The significance of such a shape-method will be enhanced if any eigenfunction or group of discrete eigenfunctions protrudes out of the continuum. When this results, the dependence of both integrals on the initial conditions will be weakened.

Another possibility is the use of a few low order time moments as the functional ratio. Time moments have the important advantage of being calculable using steady-state flux computations. For example, the first n time moments may be computed in the following manner.⁽⁹³⁾

$$H\phi^{(0)} + S(\vec{r}, \vec{v}) = 0 \quad (9.6)$$

$$H\phi^{(n)} + (n/v)\phi^{(n-1)}(\vec{r}, \vec{v}) = 0 \quad (9.7)$$

$$\bar{t}^n(\vec{r}, \vec{v}) = \phi^{(n)} / \phi^{(0)} \quad (9.8)$$

Where H is the time independent reaction rate operator, $\phi^{(0)}$ is the time integrated flux, and $\phi^{(n)}$ is defined by Eq. 9.7 as the flux due to an external source of the form $(n/v)\phi^{(n-1)}(\vec{r}, \vec{v})$. Calculations of time moments can thus be done with the aid of steady state codes providing they can accept arbitrary external sources.

The 1DF S_n transport theory code⁽⁵³⁾ has provision for a P_0 source. Thus, since the scalar flux can be punched out from a previous run, one can supply an appropriate P_0 source, $\phi^{(n-1)}(r, v)/v(E)$, for the next calculation. This procedure has been checked and found to work satisfactorily. Recently a provision was added to the code that will permit the use of an external source with any degree of anisotropy, but this has not yet been fully checked. The experimental time moments are sensitive to the poor statistical precision of the decaying flux at times long after the burst. The higher the moment the larger will be this error due to the higher weight given to it. A third theoretical approach is based on the asymptotic reactor theory and thus is limited to bare homogeneous (multiplying) systems.^(86, 94) A fourth theoretical approach, and probably the most promising one, due to its generality, is the Monte Carlo approach. Some of the theoretical approaches mentioned above will be explored during the next year.

10. STUDIES IN U^{235}

10.1 SPECTRUM MEASUREMENTS IN A U^{235} SPHERE

Spectrum measurements have been made this year in a bare near-critical, enriched U^{235} spherical reactor (APFA-III).⁽⁹⁵⁾ The geometry for these studies is illustrated in Fig. 10.1. The measurements were made at the various positions shown in the figure by inserting slugs of U^{235} into the through hole. The reactor was brought to near critical by insertion of the safety block and removal of the control and reactivity rods. This configuration was maintained throughout the studies so that the reactivity level changed as the slugs were inserted as indicated by the k_{eff} table in Fig. 10.1.

The reactor was pulsed externally by impinging the electron beam from the General Atomic Linear Accelerator onto a 3/8-in. thick disc of fansteel (tungsten alloy). The reactor and target were both air cooled. It was believed that the high multiplication of the sphere would permit the system to be analyzed later by a k calculation with the IDF code.⁽⁵³⁾ This approach was justified by previous calculations⁽⁹⁶⁾ which have shown that the neutron spectrum in such a reactor was hardly sensitive to the reactivity level between a k_{eff} of 0.93 and 1.00. Also, the calculations indicated that the spectrum was sensitive to the source characteristics only in the immediate vicinity of the source. The neutrons were extracted from the various positions in turn and timed over an evacuated flight path. In separate experiments, an NE-213 proton recoil detector⁽⁷⁹⁾ was used at 220 meters to measure the fast neutron spectra, and an NE-908 lithium glass detector (described in Section 13.3) was used at 45 meters to measure the intermediate energy spectra. The low population of neutrons at intermediate

Fig. 10.1--Geometry for spectral studies in a U^{235} sphere

energy necessitated the use of the shorter flight path. Fortunately, the system dieaways were short, thus permitting the use of this detector which does have some gamma response. The reactor and pulsed source intensities were monitored by a sulphur foil and by room return fission counters in addition, of course, to the regular reactor instrumentation. Figure 10.2 is a photograph of the over-all experimental arrangement. The data were recorded on both a TMC-201 1024 channel analyzer and on an Eldorado analyzer interfaced to a CDC-1700 on line computer.

The measured data have been reduced by means of the HECTO code⁽⁴³⁾ which subtracts background, and corrects for count rate losses and mean emission times. Figure 10.3 compares the spectrum measured at the center of the sphere with the results of a GAM II⁽⁸⁷⁾ calculation. GAM-II is an infinite medium code, but it can be used in lieu of a space dependent code for a bare critical reactor in the fundamental mode due to the separability of space and energy for such a system. (See the first fundamental theorem of reactor theory, p. 382 of Ref. 97.) This is useful because more energy detail in the spectrum can be obtained with GAM-II. The overlap of the data from the two different detection systems is fairly satisfactory. The GAM-II calculated spectrum differ little when the ENDF/B cross sections for U²³⁵⁽⁹⁸⁾ are used instead of the values due to Joanou and Drake⁽⁹⁹⁾ in GAM-II. The theory and measurement agree reasonably well except below 200 KeV, where the theory is low by an amount far outside any uncertainties in the efficiency of the lithium glass detector. This discrepancy may be due to:

1. Incorrect inelastic scattering cross sections for U²³⁵, and/or
2. Insufficient low energy neutrons in the fission spectrum,
and/or
3. Presence of higher order harmonics.)

These possible sources of error will be investigated early in the coming year.

Fig. 10. 2--Photograph of the U^{235} sphere

Fig. 10.3 Comparison of theoretical and measured neutron spectra at the center of a U^{235} sphere

The observed spectrum at the surface of the sphere is not much "harder" than the central measured values. This is surprising since previous S_n transport theory calculations,⁽⁹⁶⁾ shown in Fig. 10.4, indicate a substantial change. This is believed to be due to room return effects. Consequently future analysis of these measurements will include some representation of the room and air in the calculational geometry. Comparison of these data will also be made to the surface spectrum measurements performed previously⁽⁶⁾ on a similar U^{235} sphere.

10.2 DIEAWAY STUDIES IN U^{235} SPHERE.

Several dieaway measurements were done with the APFA III fast reactor. The purpose of these measurements was to determine the fundamental decay constant of the prompt neutrons at various control-rod conditions. This information in turn can be used to assess the reactivity worth of the control rod and to estimate the mean-emission times of the neutrons which are needed for the evaluation of the time-of-flight spectrum measurements.

In order to reduce the effect of room return neutrons and the amount of spatial harmonics, the neutron source, created by the bremsstrahlung 30 MeV electrons from the Linac beam was effectively located at the center of the APFA reactor. A 25-mil thick shield of Cd was placed around the reactor at a distance of 10 inches from it, to reduce the thermal room return. The neutron detector was positioned at a distance of 2.48 inches from the center of the reactor. This detector was a solid state detector with U^{235} fission conversion foil. The same detector and its associated electronics were used extensively in the kinetic studies performed in the U^{238} sphere and described in Section 9.

Two time analyzers were used simultaneously, one (incorporating a TAC) with 9.92 nsec per channel and the other (TMC 201 with 31.166 nsec per channel.

Fig. 10.4--Calculated angular spectra in the U^{235} sphere

The results of the first measurements are listed below in Table 10.1. These results and additional ones will be discussed in more details in the next quarterly report.

Table 10.1

RESULTS OF DIEAWAY MEASUREMENTS ON APFA III

<u>Run No.</u>	<u>C. R.^a Conditions</u>	<u>$\alpha(\text{sec}^{-1})$</u>	<u>$\pm \Delta\alpha(\text{sec}^{-1})$</u>
2	all C. R. and S. B. ^b fully inserted	3.2×10^6	0.13×10^6
3	all C. R. fully inserted S. B. - 0.25 in. withdrawn	5.3×10^6	0.3×10^6
4	all C. R. fully inserted S. B. - 0.5 in. withdrawn	7.1×10^6	0.7×10^6
5, 6	all C. R. fully inserted S. B. 0.75 in. withdrawn	1.0×10^7	0.1×10^7
1	APFA fully shutdown (all C. R. and S. B. fully withdrawn)	2.4×10^7	0.25×10^7

^aC. R. - abbreviation for Control Rods

^bS. B. - abbreviation for Safety Blocks

11. DATA DISSEMINATION

During this year, we have continued to submit tested scattering laws to the ENDF/A.⁽¹³⁾ This submission completes our development and experimental evaluation of each new theoretical scattering model. The data listed in Table 11.1 has been submitted during this year.

Table 11.1

SCATTERING DATA SUBMITTED TO ENDF/A

<u>Moderator</u>	<u>Temperatures</u>	<u>Model</u>	<u>Item</u>
H ₂ O	800°K, 1000°K	Haywood-II ⁽¹⁹⁾	S(α, β) GASKET
D ₂ O	800°K, 1000°K	Haywood ⁽⁶⁾	S(α, β) GASKET
C	1600°K, 2000°K	Young ⁽¹⁰⁰⁾	S(α, β) GASKET σ_n (elastic coherent) HEXSCAT n = 1, ..., 5.
ZrH ₂	296°K, 400°K, 500°K, 600°K, 700°K, 800°K 1000°K and 1200°K	Gaussian + Debye ⁽¹⁹⁾	σ_n (elastic incoherent) ZREND n = 1, ..., 5.

Experimental evaluation has been completed for other models developed during the past year and results will be submitted shortly. Included will be descriptions for work on benzene,⁽⁹⁾ and zirconium hydride described in Section 5. The dissemination of these data will require also the distribution of a compact and concise reference manual describing each scattering model on file. We have therefore begun the compilation of such a reference manual for our own data which is known colloquially as the "Kernel Book." In the "Kernel Book," we describe the data available for each moderator, and what model and codes have been used to compute these data. The data submitted to ENDF include thermal inelastic incoherent scattering laws and Legendre moments through P_5 of the elastic incoherent and coherent scattering by various moderators.

The function of each code and the input instructions are described in the "Kernel Book." This description is not intended to replace the more complete discussion given in the references, but it permits a simple compilation of the input data and provides examples for users. The codes have all been written in FORTRAN IV and the more important ones are or will soon be available through the Argonne Code Center. The data for each moderator are included in a loose leaf format similar to the General Atomic Spectrum Book.⁽¹⁷⁾ This permits the manual to be revised easily and thus kept up to date.

For each moderator there is a concise description of the physics model of the scattering together with the pertinent references. An illustration of the frequency spectrum used is included. Following the physics description is a listing of the card input to all the codes used to generate the ENDF data for that particular moderator. This should permit anyone to regenerate the data or modify model parameters relatively easily. Also included are tabulated values of various integral quantities deduced from the theoretical scattering law. There will also be some comments on the model and comments on the output data and its comparison to available measurements.

In addition to the compilation of the "Kernel Book" and submission of data to ENDF/A, further information is disseminated by means of the General Atomic and EARCP Spectrum Books.^(17, 18) During this year we have added the position-dependent spectra in beryllium metal at 77.4°K to the General Atomic Spectrum Book. More spectral data are forthcoming.

12. MISCELLANEOUS ANALYSES

12.1 INCLUSION OF DIFFUSIVE MOTION IN GASKET⁽⁷⁾

The theory of neutron scattering by liquids is still in a very early stage of development. Although rather sophisticated models have been proposed in the literature, none of them is truly satisfactory in fitting experimental data. In view of this situation the simplest of all these models which would satisfy the sum rules given by Placzek⁽¹⁰¹⁾ for $S(\alpha, \beta)$ and its first few moments was chosen to describe diffusive degrees of freedom in our unified code GASKET⁽⁷⁾ for thermal neutron scattering. This very simple model was formulated by Egelstaff⁽¹⁰²⁾ and leads to the formulae given in Sections 2.2 and 4. of Ref. 7. At the time of publication of this reference, the diffusive mode (Mode 2) or its combination with other modes had not yet been programmed. The coding for these modes has now been completed and in the following we report some of the corresponding details, as well as some numerical results obtained for H_2O .

First, we shall recall the basic formulae. The Fourier transform of the (nonsymmetric) scattering law for the Egelstaff model of diffusive motion is

$$\chi_2(t) = e^{2\alpha w_2 dc} \exp \left\{ -\alpha w_2 \left[G_{2 \text{ even}}(t) + i G_{2 \text{ odd}}(t) \right] \right\} \quad (12.1)$$

where

$$G_{2 \text{ even}}(t) = d\sqrt{2} \sqrt{\sqrt{(T^2 t^2 + c^2)^2 + T^2 t^2} + T^2 t^2 + T^2 t^2 + c^2} \quad (12.2)$$

and

$$G_{2 \text{ odd}}(t) = -\eta d/\sqrt{2} \sqrt{\sqrt{(T^2 t^2 + c^2)^2 + T^2 t^2} - T^2 t^2 - c^2} \quad (12.3)$$

with

$$\eta = +1 \quad \text{for } t > 0$$

$$\eta = -1 \quad \text{for } t < 0$$

In these expressions, d is the diffusion coefficient, w_2 the weight of Mode 2 (as compared to other modes present), c is an adjustable parameter, T the temperature and α is defined by the relation, $\alpha = \frac{\kappa}{2MT}$ where M is the atomic mass of the scatterer and κ the momentum transfer.

The symmetric scattering law $S(\alpha, \beta)$ for a combination of Modes 2 and 3 (isotropic vibrations with distributed frequency spectrum) is obtained from the Fourier transform of the product $X_2 X_3$. After some transformations we obtain the result,

$$S(\alpha, \beta) = S^{(1)}(\alpha, \beta) + S^{(2)}(\alpha, \beta) \quad (12.4)$$

where

$$S^{(2)}(\alpha, \beta) = \frac{\overline{D} 2\alpha w_2 d (c^2 + 1/4)^{1/2}}{\pi T [\beta^2 + (2\alpha w_2 d)^2]^{1/2}} K_1 \left\{ \left(c^2 + \frac{1}{4} \right)^{1/2} \left[\beta^2 + (2\alpha w_2 d)^2 \right] \right\}^{1/2} \quad (12.5)$$

$$S^{(1)} = \frac{e^{\beta/2\overline{D}}}{\pi} \int_0^\infty dt [Q(t) \cos \beta Tt - R(t) \sin \beta tT] \quad (12.6)$$

and with the following definitions:

$$Q(t) = \cos [\alpha \bar{F}(t)] \exp [\alpha \bar{H}t] - \cos [\alpha w_2 G_{2 \text{ odd}}(t)] \\ \cdot \exp [-\alpha w_2 G_{2 \text{ even}}(t)] \quad (12.7)$$

$$R(t) = \sin [\alpha \bar{F}(t)] \exp [\alpha \bar{H}t] + \sin [\alpha w_2 G_{2 \text{ odd}}(t)] \\ \cdot \exp [-\alpha w_2 G_{2 \text{ even}}(t)] \quad (12.8)$$

$$\bar{H}(t) = -w_2 G_{2 \text{ even}}(t) + H(t) \quad (12.9)$$

$$\bar{F}(t) = -w_2 G_{2 \text{ odd}}(t) + F(t) \quad (12.10)$$

$$\bar{D} = \exp \{ \alpha [2w_2 \text{dc} - w_3 \gamma(0)] \} \quad (12.11)$$

$$H(t) = w_3 T \int_0^{\infty} f(\omega) \coth \frac{\omega}{2T} \cos \omega t \frac{d\omega}{\omega} \quad (12.12)$$

$$F(t) = w_3 T \int_0^{\infty} f(\omega) \sin \omega t \frac{d\omega}{\omega} \quad (12.13)$$

$$\gamma(0) = \frac{H(0)}{w_3} \text{ (Debye Waller integral)} \quad (12.14)$$

$K_1(x)$ is the modified Bessel function of the second kind and first order. One of the conveniences of the model is the possibility of calculating the zero-phonon term $S^{(2)}$ in closed form. This is important since this term usually is a rapidly varying function of β .

Since the parameter c is generally large, of the order of 100, K_1 is generally calculated from the first three terms of its asymptotic expansion.

$$K_1(x) \sim e^{-x} f(x) \quad (12.15)$$

$$f(x) = \sqrt{\frac{\pi}{2x}} \left[1 + \frac{1}{x} \left(\frac{3}{8} - \frac{15}{128x} \right) \right] \quad (12.16)$$

For arguments smaller than a given input number, however, $K_1(x)$ is calculated by a recursive routine. When K_1 is calculated from its asymptotic series $S^{(2)}$ is calculated in the form.

$$S_2(\alpha, \beta) = \frac{2\alpha w_2 d(c^2 + 1/4) e^{y-x} f(x)}{\pi T x} \quad (12.17)$$

with

$$x = (c^2 + 1/4)^{1/2} \left[\beta^2 + (2\alpha w_2 d)^2 \right]^{1/2} \quad (12.18)$$

and

$$e^y = \bar{D}.$$

This avoids machine overflow of the exponential function since although $\bar{D}$ and e^x are individually large, their ratio e^{y-x} is always within the machine range. For similar reasons, the factor $\bar{D}$ is absorbed into Q and R in the evaluation of $S^{(1)}$ by defining the quantities

$$Q'(t) = e^{y - \alpha w_2 G_{2 \text{ even}}(t)} \left\{ \cos[\alpha \bar{F}(t)] e^{\alpha w_3 H(t)} - \cos[\alpha w_2 G_{2 \text{ odd}}(t)] \right\} \quad (12.19)$$

$$R'(t) = e^{y - \alpha w_2 G_{2 \text{ even}}(t)} \left\{ \sin[\alpha \bar{F}(t)] e^{\alpha w_3 H(t)} + \sin[\alpha w_2 G_{2 \text{ odd}}(t)] \right\} \quad (12.20)$$

Another numerical difficulty occurs when evaluating $G_{2 \text{ odd}}(t)$ for small values of tT and large values of d and c . Hence, when Tt is smaller than a given input number, the innermost square root of $G_{2 \text{ odd}}$ is expanded

in a power series leading to the following approximate representation.

$$G_{2 \text{ odd}}(t) \cong -\eta d \sqrt{2} T t \sqrt{\frac{1}{2} \frac{1}{T^2 t^2 + c^2} - \frac{1}{8} \frac{T^2 t^2}{(T^2 t^2 + c^2)^3} + \frac{1}{16} \frac{T^4 t^4}{(T^2 t^2 + c^2)^5}} \quad (12.21)$$

Since free translations and diffusive motions are incompatible, the program does not allow for $w_1 \neq 0$ and $w_2 \neq 0$ at the same time. The flow of the program for convolution with discrete modes of vibration (Mode 5) is the same in either case ($w_1 \neq 0$ or $w_2 \neq 0$); the only difference is the form of $S^{(2)}$ supplied to the convolution routines.

The new option for diffusive motion of the code was first tried out on a water model. The parameters used were the same as for the Haywood II model with $w_2 = .055$ replacing the free translations and with $d = c - 50$, (d and c should be equal if Placzek sum rule for the first moment of $S(\alpha, \beta)$ is to be satisfied). The comparison with the original calculation ($w_1 = .055$) is shown in Fig. 12.1 for $\alpha = .2$. The curves are nearly identical over most of the range of β . The largest difference occurs around $\beta = .5$ and is due to $S^{(2)}$. For larger α , there is even less difference. The similarity of the results is due to the large values of $d \approx c$. This makes the argument of the Bessel function in $S^{(2)}$ large and hence, using the asymptotic series for K_1 and expanding the square root in its argument

$$\left[\beta^2 + (2w_2 d \alpha)^2 \right]^{1/2} \sim 2w_2 d \alpha \left[1 + \frac{1}{2} \left(\frac{\beta}{2w_2 d \alpha} \right)^2 \right]$$

we get, after neglecting terms in $(\beta/2w_2 d \alpha)^2$

$$S^{(2)} = \frac{1}{\sqrt{4\pi \alpha w_2 T^2}} \exp \left(-\frac{\beta^2}{4\alpha w_1} \right) \quad (12.22)$$

Fig. 12.1--Comparison of diffusive and free recoil treatments of translational modes in H_2O

which differs from the free gas result only by a factor

$$\exp\left(-\frac{w_2 \alpha}{4}\right)$$

which for the mentioned values of w_2 and α is practically 1.

12.2 APPLICATION OF NONLINEAR PROGRAMMING TO CROSS SECTION ANALYSIS

The differential elastic scattering cross section $\sigma(\mu)$ is frequently represented as a sum of Legendre polynomials in neutronic calculations. One commonly used method of obtaining a set of Legendre coefficients from a given set of experimental points is the method of least squares. This method, as well as other methods, sometimes leads to negative values of $\sigma(\mu)$ whenever a reasonable number, say less than fifteen, of Legendre coefficients are used. This is particularly true at high energies and for heavy scattering nuclei because of the extreme peaking of the differential cross section in the forward direction.

In order to avoid the difficulties associated with negative cross sections, it is desirable to impose constraints on the method of least squares, so that the Legendre expansion predicts only positive cross sections. The formulation then leads naturally to a quadratic programming problem, a special case of the more general nonlinear programming problem.⁽¹⁰³⁾

In the least squares method, the quantity

$$E = \sum_{j=1}^N \left[\sigma_j - \sigma(\mu_j) \right]^2 \quad (12.23)$$

is minimized. In Eq. 12.1, $\sigma(\mu)$ is defined by the expansion:

$$\sigma(\mu) = \sigma_s \sum_{\ell=0}^n \frac{2\ell+1}{2} f_{\ell} P_{\ell}(\mu) \quad (12.24)$$

The minimizing of E leads to a set of Legendre coefficients f_ℓ . Another method which is used frequently is to obtain f_ℓ directly from the integral,

$$f_\ell = \frac{1}{\sigma_s} \int_{-1}^1 \sigma_e(\mu) P_\ell(\mu) d\mu \quad (12.25)$$

where $\sigma_e(\mu)$ is assumed to be a simple continuous function (usually straight line segments) which passes through the experimental points σ_j . With either method, Eq. 12.24 is used to compute the cross section for all angles once the Legendre coefficients have been found. When the number of experimental points, N , is very large and the entire μ interval $[-1, 1]$ is covered with experimental points the two methods predict the same values for f_ℓ . For the usual case, however, the two methods can give significantly different sets of coefficients.

In practice, it is possible that a set of coefficients f_ℓ will predict negative values of $\sigma(\mu)$ if these are evaluated from Eq. 12.24. This is true for both of the methods of computing f_ℓ described above because of the necessity of making the truncation coefficient n finite. If $\sigma(\mu)$ is highly peaked at some angle, this problem becomes particularly serious, for then the negative values of $\sigma(\mu)$ persist even for large values of n . For heavy isotopes, like U^{238} , forward peaking of the angular distribution of elastic scattering is very pronounced for all neutron energies in excess of 3 MeV or so. Consequently, large intervals of negative cross sections persist for $n = 9$ (the number used for U^{238} in the ENDF/B data file)⁽⁸¹⁾ and even larger values. In general, the magnitude of the cross section is not large when σ attains negative values and $n \geq 9$. But negative cross sections can be more than a mere annoyance; they can lead to negative transfer coefficients in computer codes which evaluate neutron spectra, with unpredictable consequences. In Monte Carlo codes they can lead to negative probabilities, negative estimates of physically positive quantities or, sometimes mercifully, failure of the computer program to execute. In order to circumvent these difficulties, it is common to reassign a value to a negative cross

section of either zero or its absolute value. Such manipulations not only are unaesthetic but also have unpredictable consequences. Thus, there is an incentive to find a method for computing Legendre coefficients which predict positive cross sections in addition to being accurate. To achieve this, we shall use the method of least squares but we shall add a number of constraints.

In principle, then, we look for coefficients f_ℓ that minimize E of Eq. 12.23, but in addition satisfy the requirement that

$$\sum_{\ell=0}^n \frac{2\ell+1}{2} f_\ell P_\ell(\mu) \geq 0 \quad -1 \leq \mu \leq 1. \quad (12.26)$$

In addition, Eq. 12.25 suggests the additional constraints.

$$\begin{aligned} f_0 &\geq 0, \\ f_0 &\geq |f_\ell| \quad \ell = 1, 2, \dots, n \end{aligned} \quad (12.27)$$

At this time, no method has been found that will find a set of f_ℓ , in a systematic manner, which will minimize E while satisfying Eqs. 12.26 and 12.27. Irving, et al., ⁽¹⁰⁴⁾ have solved a more restricted problem; namely, given a set of f_ℓ satisfying Eq. 12.27 they find additional criteria that are necessary and sufficient to assure that Eq. 12.26 is satisfied. Now if, instead of Eq. 12.26, we impose the constraint

$$\sum_{\ell=0}^n \frac{2\ell+1}{2} f_\ell P_\ell(\mu_j^*) \geq 0 \quad j = 0, 1, 2, \dots, M, \quad (12.28)$$

a solution can be found by the techniques of nonlinear programming. ⁽¹⁰³⁾

As M is increased, Eq. 12.28 approaches Eq. 12.26. Furthermore, in several cases a judicious choice of the μ_j^* in Eq. 12.28 assures that if Eq. 12.28 is satisfied, then so is Eq. 12.26. In order to transform our problem, namely the minimizing of E in Eq. 12.23 subject to the constraints

of Eqs. 12.27 and 12.28, into the canonical form of the nonlinear programming problem we proceed as follows: First make the linear transformation,

$$f_{\ell} = \sum_{k=0}^n T_{\ell k} x_k, \quad (12.29)$$

where

$$T_{0k} = 1, \quad k = 0, 1, \dots, n \quad (12.29a)$$

and

$$T_{\ell k} = 1 - 2\delta_{\ell k}, \quad \ell \geq 1, k = 0, 1, \dots, n. \quad (12.29b)$$

In Eq. 12.29b, $\delta_{\ell k}$ is the Kronecker δ .

In expanded form, this takes the form

$$f_0 = x_0 + x_1 + x_2 + x_3 + \dots$$

$$f_1 = x_0 - x_1 + x_2 + x_3 + \dots$$

(12.29c)

$$f_2 = x_0 + x_1 - x_2 + x_3 + \dots$$

$$f_3 = x_0 + x_1 + x_2 - x_3 + \dots$$

Insertion of Eq. 12.29 into 12.25 gives

$$E = \sum_{j=i}^N \left[\sigma_j - \sum_{\ell=0}^n \frac{2\ell+1}{2} P_{\ell}(\mu_j) \sum_{k=0}^n T_{\ell k} x_k \right]^2 \quad (12.30)$$

and, more important, Eq. 12.27 transforms to

$$x_{\ell} \geq 0 \quad \ell = 1, \dots, n. \quad (12.31a)$$

It is desirable that the constraints we place on the x_ℓ be consistent with those which are imposed on the f_ℓ by Eq. 12.27. The nonlinear programming method of solution which we will use satisfies the constraint

$$x_\ell \geq 0 \quad \ell = 0, 1, \dots, n. \quad (12.31b)$$

This is slightly more restrictive than that imposed by Eq. 12.31a and, equivalently, by Eq. 12.27. Nevertheless, it appears that satisfactory solutions can be found within the domain of Eq. 12.31b.

Equation 12.30 may be written as

$$E = \sum_j \left\{ \sigma_j^2 - 2\sigma_j \sum_{k=0}^n x_k \sum_{\ell=0}^n \frac{2\ell+1}{2} T_{\ell k} P_\ell(\mu_j) \right. \\ \left. + \sum_{k=0}^n \sum_{\ell=0}^n \sum_{m=0}^n \sum_{i=0}^n x_k x_m \frac{2\ell+1}{2} \frac{2i+1}{2} T_{\ell k} T_{im} P_\ell(\mu_j) P_i(\mu_j) \right\} \quad (12.32)$$

Now, if we define

$$Z = -E + \sum_j \sigma_j^2, \quad (12.33)$$

$$c_k = 2 \sum_{\ell=0}^n \frac{2\ell+1}{2} T_{\ell k} \sum_j \sigma_j P_\ell(\mu_j), \quad k = 0, 1, \dots, n \quad (12.34)$$

and

$$d_{km} = - \sum_{\ell=0}^n \sum_{i=0}^n \frac{2\ell+1}{2} \frac{2i+1}{2} T_{\ell k} T_{im} \sum_j P_\ell(\mu_j) P_i(\mu_j), \quad (12.35)$$

$$k = 0, 1, \dots, n$$

$$m = 0, 1, \dots, n,$$

we have

$$Z = \sum_k c_k x_k + \sum_k \sum_m x_k d_{km} x_m \quad (12.36)$$

In matrix notation,

$$Z = CX + X^T DX. \quad (12.37)$$

From Eq. 12.33, we observe that the problem of finding a minimum value of E is equivalent to finding a maximum for Z .

Insertion of Eq. 12.29 into Eq. 12.28 yields

$$\sum_{\ell=0}^n \frac{2\ell+1}{2} P_{\ell}(\mu_j^*) \sum_{K=0}^n T_{\ell K} x_K \geq 0 \quad (12.38)$$

Define

$$A_{ik} = \sum_{\ell=0}^n \frac{2\ell+1}{2} P_{\ell}(\mu_i^*) T_{\ell k} \quad (12.39)$$

so that, in matrix form, Eq. 12.38 takes the form

$$AX \geq 0 \quad (12.40)$$

Equation 12.31b may, of course, also be written in matrix form as

$$X \geq 0 \quad (12.41)$$

Equations 12.37, 12.40, and 12.41 form a quadratic programming program, a special case of the more general nonlinear programming problem. Before proceeding to the solution of the problem it is convenient to introduce "surplus" variables⁽¹⁰³⁾ so that the inequality is removed from Eq. 12.40; that is, with the surplus variables, Eq. 12.40 takes the form

$$AX = 0 \quad (12.42)$$

With the introduction of the surplus variables, our matrices have the expanded form:

$$C = \left(\overbrace{c_0 \ c_1 \ \dots \ c_n}^{n+1} \quad \overbrace{0 \ \dots \ 0}^{M+1} \right)$$

$$X^T = (x_0 \ x_1 \ \dots \ x_n \quad x_{n+1} \ \dots \ x_{n+M+1})$$

$$D = \left(\begin{array}{cc} \overbrace{d_{00} \ d_{01} \ \dots \ d_{0n}}^{n+1} & \overbrace{\phantom{d_{00} \ d_{01} \ \dots \ d_{0n}}}^{M+1} \\ \vdots & \vdots \\ \overbrace{d_{no} \ \dots \ d_{nn}}^{n+1} & \overbrace{\phantom{d_{no} \ \dots \ d_{nn}}}^{M+1} \\ \hline & 0 \end{array} \right) \begin{array}{l} n+1 \\ \\ M+1 \end{array}$$

$$A = \left(\begin{array}{cc} \overbrace{A_{00} \ A_{01} \ \dots \ A_{0n}}^{n+1} & \overbrace{-1 \ 0 \ 0 \ \dots \ 0}^{M+1} \\ \vdots & \vdots \\ \overbrace{A_{M0} \ \dots \ A_{Mn}}^{n+1} & \overbrace{0 \ \dots \ -1}^{M+1} \end{array} \right) \begin{array}{l} \\ \\ M+1 \end{array}$$

The dimensions of the matrices are indicated along the edges of the matrices. In Ref. 103, it is shown that if D is negative definite or semi-definite, the quadratic programming problem can be transformed into a

problem which is almost straightforward as the linear programming problem. In particular, the transformed problem is

$$QW = f; W \geq 0; X^T V = 0; \max P = - \sum_j u_j \quad (12.43)$$

This problem is linear except for the restriction $X^T V = 0$. The matrix Q in Eq. (2) is defined as

$$Q = \begin{bmatrix} A & 0 & 0 & 0 & 0 \\ 2D & -A^T & A^T & I & E \end{bmatrix} \quad (12.44)$$

where I is a unit matrix and E is a diagonal matrix whose elements are $\Delta_j = \pm 1$. $\Delta_j = 1$ if $c_j \leq 0$, $\Delta_j = -1$ if $c_j > 0$. The matrix W is

$$W = [X, \zeta, \xi, V, u] \quad (12.45)$$

and f is defined by

$$f = [0, -C^T]. \quad (12.46)$$

The length of the vectors X , V , and u is $n + m + 2$, that of ζ and ξ is $m + 1$, so that the total length of W is $3n + 5m + 8$. Equation 12.43 can be solved by the revised Simplex method with one modification to assure that the relation $X^T V = 0$ is satisfied. ⁽¹⁰³⁾

A computer program, QUAD, which is based on the theory described above, has been written and is in the final stages of debugging.

A simple test problem has been run successfully, and the results are shown in Fig. 12.2. The data points in Table 12.1 were given as input. A parabola which passes through these points gives negative values in the interval between roughly $\mu = -0.36$ and $\mu = -0.62$. A parabola which passes

Fig. 12.2 Constrained and unconstrained least squares fit to the data points in table 12.1

near the data points, but does not go negative at the points designated by the arrows, namely $\mu = 1.0, -0.6, -0.5$ and -0.4 has been computed by QUAD is also shown. The fit is still good and the constraints are satisfied. The curve still dips very slightly negative, but this can be changed by adding more constraint points.

Table 12.1
SAMPLE POINTS FOR
TESTING THE CODE QUAD

μ	σ
-1	0.23
0	0.23
1	2.23

A more rigorous test example is shown in Fig. 12.3, which shows the elastic scattering cross section of Pu^{240} at 15 MeV and best low order polynomial approximations which are constrained to yield positive cross sections. The Pu^{240} cross section was obtained from an optical model calculation; ⁽¹⁰⁵⁾ it represents cross section as peaked as any likely to be encountered in reactor applications.

Figure 12.3 which emphasizes the low-valued cross section range, reveals that positive cross sections are obtained even from low order polynomial approximations. This certainly is not the case for a standard least squares analysis of such a peaked cross section. The over-all quality of the fit, for a fixed polynomial approximation, is not so good for our analysis as it is for the standard analysis which imposes no constraints. In some applications, however, the elimination of negative cross sections is well worth this cost. Of course, in order to obtain an over-good fit of the Pu^{240} cross section shown in Fig. 12.3, a high degree polynomial approximation is required, regardless of the method chosen for the fitting.

Fig. 12.3--Everywhere positive law order polynomial approximation to a highly peaked cross section

12.3 CORRECTION FOR FINITE LENGTH OF FLIGHT PATH IN SINGLE DIFFERENTIAL CROSS SECTIONS

The effect of having a finite length for the flight path after the sample in a single differential scattering experiment was described in a previous report.⁽⁶⁾ A factor C_p was derived to account for this effect, defined as follows:

$$C_p = \frac{\Delta \bar{E}_0 \varphi(\bar{E}_0) \int_0^{\infty} \sigma(\bar{E}_0, E_1, \theta) dE_1}{\int_{\Gamma} \varphi(E_0) \sigma(E_0, E_1, \theta) dE_0 dE_1} \quad (12.47)$$

where $\sigma(E_0, E_1, \theta)$ is the double differential cross section, $\varphi(E_0)$ is the incident spectrum, and Γ is the region of the plane $E_0 E_1$ corresponding to a time channel.

The C_p factor was derived by performing a double integration numerically over the variables E_0 and E_1 . The integral was evaluated over a region bound by curved lines, and an extremely fine mesh was required in the integration process to avoid numerical errors. A different way to evaluate the integral, which is faster and gives more exact results, is now described.

We make a transformation from the variables E_0 and E_1 , respectively incident and final energies of the neutron, to the variables t_0 and t , respectively time of flight over the distance ℓ_0 and total time of flight over the distance $\ell_0 + \ell_1$.

The transformation is defined by the equations:

$$\begin{cases} \bar{E}_0 = \frac{m}{2} \frac{t_0^2}{t_0} \\ \bar{E}_1 = \frac{m}{2} \frac{t_1^2}{(t-t_0)^2} \end{cases} \quad (12.48)$$

where m is the neutron mass.

The integral in the denominator of Eq. 12.47 is simplified by the use of this time transformation. The C_p factor becomes:

$$C_p = \frac{m(t_0+t_1)^2 \varphi(\bar{E}_0) \int_0^\infty \sigma(\bar{E}_0, E_1, \theta) dE_1}{t^3 \int_0^t \varphi_1(t_0) \sigma_1(t_0, t-t_0, \theta) |J| dt_0} \quad (12.49)$$

where $\varphi_1(t_0)$ and $\sigma_1(t_0, t-t_0, \theta)$ are the incident spectrum and the cross section expressed as a function of time, and J is the Jacobian of the transformation. Here $\bar{E}_0$ is connected to t by

$$\bar{E}_0 = \frac{m}{2} \frac{(t_0+t_1)^2}{t^2} \quad (12.50)$$

The integral in the denominator of Eq. 12.49 can be evaluated more accurately and in a faster way than the corresponding integral in Eq. 12.47. However, one has to be very careful because the Jacobian presents singularities at $t_0 = 0$ and $t_0 = t$. A numerical method which treats the integration in two different ways when approaching the singularities has been set up and included in the code FLAME.

Figure 12.4 shows the C_p factor calculated with the time integration method for $ZrH_{1.85}$ at 90° scattering angle. As is expected, the factor is very near to unity, except for energies near the first oscillator level (0.137 eV) where it reaches a value of about 0.85. The effect of including the C_p factor in the treatment of the data is that of making the dips in the single differential cross section of $ZrH_{1.85}$ more pronounced. Experimental evidence for the correctness of this effect has been observed. (see Section 5.3).

Fig. 12.4--Variation of correction factor C_p with incident neutron energy for zirconium hydride

13. IMPROVEMENT IN LINAC AND EXPERIMENTAL CAPABILITIES

13.1 LINAC FACILITY IMPROVEMENTS

During this year the upgrading of the General Atomic LINAC facility has been continued. The single stage and the three-stage machines can now be run separately or in tandem as a routine operation. This is possible because the injector for the three-stage machine is located permanently off axis. When this injector is used, its output is put on axis by means of a small bending magnet. A closed-circuit cooling system has been installed in place of the old open circuit system. Two of the waveguides have been replaced by improved iris-coupled constant gradient accelerating structures having higher power ratings (25 MW). The high power modulators that were under construction last year have been completed. Output of the present machine is limited by the capabilities of the power supplies. The remaining modulators will be rebuilt and upgraded when they are moved to a lower radiation environment outside the accelerator room. The peak beam power conditions obtained with the four-stage machine have been materially improved both in current and in the electron energy.

A new cell is to be constructed adjacent to the single-stage machine during the next six months. This cell will have provision for a short flight path. The cell is expected to be used predominantly for studies of transient radiation effects, electron scattering, and neutron photo-fission thresholds. Service irradiations are expected to be facilitated with this cell.

The 225-meter flight path and fast spectrum cell (FSC) were installed last year and have been put into use. This flight path became

operational when the vacuum pumps were mounted and installed at their final positions, and when the collimators were constructed and put into place. The spectrum measurements on APFA-III described in Section 10, utilized both the FSC and the 220-meter flight path and demonstrated a significant improvement in our capabilities for measuring spectra from multiplying assemblies over a wide range of neutron energies. These capabilities are being further extended by the installation of a split bed assembly machine in the fast spectrum cell. This will permit the study of reactor systems of interest to the fast breeder reactor program, including ZPR-III-type assemblies.

Other improvements to our experimental capabilities include better measurement of intermediate energy neutrons with the detector described in Sections 13.2 and 13.3. In addition, the CDC-1700 computer was received during this year; its capabilities and operational experience are described in Section 13.4. We are also improving the electronics in the data-taking room by installation of more solid state components and removal of the older tube-type equipment. This has substantially enhanced our ability to perform experiments requiring fast timing and good resolution. In addition, we are making provision for two independent setups that will permit the logic units to be wired up and tested off-line and allow us to consider multiplexing the accelerator.

13.2 INTERMEDIATE ENERGY NEUTRON DETECTOR

An intermediate energy neutron detector (IED) has been designed and constructed at General Atomic for the purpose of measuring neutron spectra in the intermediate energy range. The geometry of this detector and its development has been described in previous reports. (6, 58, 96, 106). A complete report on this detector, which is to be released shortly, will include all the details of the design and operation. Consequently, in this section we will discuss briefly the detector philosophy and its development during the past year.

The importance of this detector came from the need to measure intermediate energy neutron spectra from fast multiplying assemblies. The requirements for the detector then became reasonable timing resolution (30 nsecs), high sensitivity to neutrons, and low sensitivity to gamma rays. These conditions would be met by surrounding a large conversion (n, γ) plate with an organic fluor capable of absorbing a significant fraction of the energy of the resulting gamma rays. By accepting counts which result in the deposition of gamma-ray energies greater than 2 or 3 MeV and by requiring coincidences between adjacent halves of the fluor, rejection of background gammas would be easily achieved. The detector was constructed around this design and was developed during the past year. Figure 13.1 is a photograph of the detector during construction.

During the first part of this year, U^{235} was used as a conversion material. An attempt was made to calibrate this detector by comparison to other detectors. In addition, the IED in that form was used to study the spectra in the 20-in. diam. U^{238} sphere (Section 8). However, these studies revealed that neutrons, both fission and scattered neutrons, were being thermalized in the organic fluor and being reabsorbed at a later time in the conversion plate. Consequently both calibration and spectral data were rejected. These faults have been remedied by the introduction of B^{10} shielding and a nonfissioning conversion plate. The new conversion plate contains a mixture of europium oxide, terbium oxide, and tantalum oxide in the isotopic ratio Eu:Tb:Ta of 3:1:1. This mixture was designed to give a fairly smooth absorption probability in the intermediate energy range on the basis of the Garrison⁽¹⁰⁷⁾ data.

The IED has been operated with the improved conversion plate and shielding and has been compared to the NE-213, $^{(79)}B_4C^{(109)}$ and lithium glass detectors. The latter detector is described in Section 13.3. The IED was found to have an excellent discrimination against background compared to these other detectors. However, the sensitivity was not as high as anticipated. It is believed that this was a consequence of setting timing

Fig. 13.1--Photograph of the intermediate energy
neutron detector (IED) during construction

coincidence requirements that were overly stringent and setting too high a bias on the energy deposition in each half of the fluor. The timing requirements were subsequently relaxed and a gain of 4 in efficiency was then obtained. It has been found necessary for the total energy absorbed to be greater than 2.2 MeV, which is the gamma-ray energy from absorption of a thermal neutron by hydrogen. It appeared that an improved efficiency could be obtained by demanding a 2.4 MeV bias on the sum of the output from the two halves instead of a 1.2 MeV bias on each half separately. This approach has been attempted but further timing problems have been encountered which are now being examined.

In summary, this detector is being developed satisfactorily although it is taking longer than we anticipated. However, it already shows promise of meeting its expectations. We plan to calibrate the detector and move it shortly to the 220-meter flight path where it will be used to study neutron spectra from fast multiplying assemblies of importance to the fast breeder reactor program.

13.3 LITHIUM GLASS DETECTOR

The new intermediate energy detector (IED) described in Section 13.2 promises to give a fairly high efficiency with a very low gamma-to-neutron response ratio. However, this detector will be difficult to calibrate other than by using it to measure a known spectrum or by inter-comparison to a calibrated detector. The IED is too bulky to be transported to another facility having an absolute flux device; moreover its geometry does not permit a simple description for computation by a Monte Carlo code. We have been reluctant to rely only on the B_4C detector⁽¹⁰⁸⁾ as an intermediate standard and have therefore purchased a lithium glass detector to provide an alternate standard.

The detector comprises a 5-in. diam. by 1/2-in. thick NE-908 lithium glass scintillator. This scintillator is coupled with Dow-Corning silicon grease to a quartz light pipe of the same dimensions as the lithium

glass. This in turn, is coupled to a XP-1040 photomultiplier tube, whose focus, cathode, and first dynode potentials have been adjusted to give maximum output and near minimum energy resolution. It is claimed that this type of detector (NE-908) provides, in addition to the energy discrimination that is normally used with these lithium glasses, some discrimination against gamma rays by means of the difference in their pulse shape response. However, we were unable to find any such pulse shape discrimination capabilities in our detector and have therefore used it with energy discrimination only. Figure 13.2 illustrates the electronics block diagram in which this detector was used for the studies of the U^{238} and U^{235} spheres described respectively in Sections 8.2 and 10.1. An attempt was made to use a linear gate with this system in order to eliminate gamma flash overload of the amplifier. The gate feedthrough was, however, found to be as much of a problem as the gamma flash so that the linear gate was not used at all. The response of the detector to a Po-Be source is shown in Fig. 13.3. The energy resolution, (FWHM), is found to be about 47% and biasing in the valley essentially eliminates counting gamma rays whose energy is lower than 250 keV.

The efficiency of the detector is to be calculated by the O5R Monte Carlo code.⁽¹⁰⁹⁾ This requires an accurate knowledge of the composition of the scintillator, particularly the Li^6 number density. In view of the importance of these quantities and because our previous experience indicated that the true lithium composition could be at variance with the manufacturer's specification, transmission measurements were performed at various positions across the glass. These studies were made in a similar manner to the total cross section measurements, described in Section 4.2, and used a procedure which is described fully in Ref. 6. In essence, the procedure consists of describing the transmission through the glass by $1/v$ absorption and purely potential scattering. Use of the 2200-m cross section for Li^6 of 945 barns⁽³⁰⁾ allows the value of $\Sigma_a T(Li^6)$ to be determined to within 1/2%. Figure 13.4 shows the energy variation

Fig. 13.2--Electronic Block Diagram incorporating the NE-908 lithium glass detector

Fig. 13.3--Response of the lithium glass detection system to a Po-Be source

Fig. 13.4--Energy dependence of the transmission through the NE-908 lithium glass

of the transmission at the glass center. The lithium composition for this particular glass was found to be uniform and equal to the specified composition of 7.8%. The resulting compositions and geometry, given in Fig. 13.5, are therefore to be used in the efficiency computation.

An interim efficiency curve for this detector has been estimated in the following way. The efficiency was calculated up to 10 keV by a simple code whose formalism is described in Ref. 6, p. 169. This code computes successive collision absorption terms based on isotropic scattering in lab coordinates with no energy transfer permitted. Source terms for tertiary and higher collisions are based on a fundamental mode neutron distribution. Although quite crude, the code is expected to give an efficiency within 20% of the true value at 1 keV. Above 1 keV, the calculations and measurements on a similar lithium glass detector due to Wattecamps⁽¹¹⁰⁾ have been used. In essence, the shape of Wattecamps efficiency curve has been retained and normalized to our calculated values between 1 and 10 keV. The resulting values have been used in the U²³⁵ and U²³⁸ studies are given in Table 13.1. Preliminary O5R calculations⁽¹¹¹⁾ indicate a remarkable agreement with these interim values at 2 MeV and 225 keV.

Table 13.1

TABULATED ESTIMATE OF THE EFFICIENCY OF THE 5-IN. DIAM
NE-908 LITHIUM GLASS DETECTOR

<u>Energy (eV)</u>	<u>Efficiency</u>	<u>Energy (eV)</u>	<u>Efficiency</u>	<u>Energy (eV)</u>	<u>Efficiency</u>
1.000-4	0.987	6.000-1	0.96555	2.046+3	0.0921
1.500-4	0.987	8.000-1	0.95566	2.591+3	0.0812
2.000-4	0.987	1.000+0	0.94550	3.293+3	0.0711
3.000-4	0.987	1.500+0	0.92037	4.188+3	0.0629
4.000-4	0.987	2.000+0	0.89681	5.309+3	0.0561
6.000-4	0.987	3.000+0	0.85537	6.730+3	0.0494
8.000-4	0.987	4.000+0	0.82048	8.560+3	0.0441
1.000-3	0.987	6.000+0	0.76478	1.000+4	0.0411

Table 13.1 (Continued)

<u>Energy (eV)</u>	<u>Efficiency</u>	<u>Energy (eV)</u>	<u>Efficiency</u>	<u>Energy (eV)</u>	<u>Efficiency</u>
1.500-3	0.987	8.000+0	0.72166	1.270+4	0.0362
2.000-3	0.987	1.000+1	0.68676	1.611+4	0.0322
3.000-3	0.987	1.500+1	0.62148	2.046+4	0.0288
4.000-3	0.987	2.000+1	0.57473	2.591+4	0.0255
6.000-3	0.987	3.000+1	0.50981	3.293+4	0.0231
8.000-3	0.987	4.000+1	0.46524	4.188+4	0.0211
1.000-2	0.987	6.000+1	0.40556	5.309+4	0.0196
1.500-2	0.987	8.000+1	0.36591	6.730+4	0.0188
2.000-2	0.987	1.000+2	0.33687	8.560+4	0.0190
3.000-2	0.987	1.500+2	0.28816	1.000+5	0.0196
4.000-2	0.987	2.000+2	0.25684	1.270+5	0.0216
6.000-2	0.987	3.000+2	0.21723	1.611+5	0.0281
8.000-2	0.987	4.000+2	0.19224	1.915+5	0.0382
1.000-1	0.98694	6.000+2	0.16114	2.046+5	0.0469
1.500-1	0.98476	8.000+2	0.14180	2.316+5	0.0637
2.000-1	0.98278	1.000+3	0.12825	2.591+5	0.0706
3.000-1	0.97886	1.270+3	0.1142	2.924+5	0.0573
4.000-1	0.97470	1.611+3	0.1038	3.293+5	0.0436
4.188+5	0.0249	1.611+6	0.0064	5.309+6	0.0036
5.309+5	0.0136	2.046+6	0.0058	6.730+6	0.0032
6.730+5	0.0101	2.591+6	0.0052	8.560+6	0.0029
8.560+5	0.0088	3.293+6	0.0046	1.000+6	0.0027
1.000+6	0.0080	4.188+6	0.0041	1.500+6	0.0024
1.270+6	0.0071

ITEM	NO. DENSITIES
	ATOMS/BARN-CM
① ALUMINUM HOLDER	Al 0.0602
② ALUMINUM FOIL	
③ LITHIUM GLASS NE-908	Li ⁶ 0.017552
	Li ⁷ 0.000804
	Si 0.018215
	Al 0.001418
	Mg 0.000148
	Ce 0.000127
④ QUARTZ (LIGHT PIPE - PM TUBE FACE)	O 0.048074
	Si 0.022032
	O 0.044064

Fig. 13.5--Geometry for calculating the efficiency of the NE-908 lithium glass detector

13.4 ON-LINE COMPUTER

A CDC-1700 computer has been purchased under this program for use at the linear accelerator facility as an on-line data acquisition system for fast spectral studies. The computer was delivered in April 1967, and has been accepted. Some of the features of this computer are as follows:

1. 12-K word magnetic core memory size
2. 16 bits/word, and one parity bit and one memory protect bit for each word in memory.
3. 1.1- μ sec memory cycle time
4. 14 interrupt data channels, priority under program control.
5. 1.25×10^6 words storage in a magnetic disc-pack which is manually removable.

A block diagram and a photograph of the computer data acquisition system are shown in Figs. 13.6 and 13.7 respectively. The capability of high-speed data acquisition coupled with the large storage area in the magnetic disc allows simultaneous storage of several time-of-flight spectra. In addition, the use of a dual ADC (analog-to-digital converter) permits multiparameter data to be acquired and stored in a convenient flexible fashion. Some data analysis is also possible immediately after a LINAC data run so that preliminary results are available to the experimenter.

The basic software supplied by Control Data Corporation consists of an operating system (called The Utility System, which does not use the disc), an assembler, a FORTRAN compiler, the object package for executing programs generated by the compiler, and a few utility routines. These have been modified at General Atomic so that the compiler and a library of basic programs are kept on the disc and can be loaded quickly - in a few milliseconds - rather than 15 minutes for the utility system or

Fig. 13.6--Block diagram of the data acquisition system designed around the CDC-1700 computer

Fig. 13.7--CDC-1700 computer with interfacing equipment

about four hours for the FORTRAN compiler. Compiler-generated programs use the utility package for performing floating point arithmetic, input-output control and conversion from internal to external representation, and function evaluation. The normal procedure for generating a program consists of producing a relocatable binary program tape, loading this tape and all necessary subroutines with the relocating binary loader and punching an absolute binary tape which is an exact image of the loaded program and all its subroutines. This absolute binary tape is then used for reloading the program on machines with fast tape readers. Our machine has an extremely slow reader: it would take an hour to load just the FORTRAN object package in relocatable form, and perhaps 40 minutes to load the absolute binary tape punched out for later use. Relocatable tapes are therefore always used as input. The object package has been loaded into the first part of core available, and copied onto the disc. To load a program which uses the object package, a preliminary tape is read which reserves the space needed by the object package in the core, makes the entry points to all the subroutines in the object package available to the loader, and finally reads the object package from the disc and transfers control to the main program for execution. This extra tape loads in about one minute.

Experience with the utility system FORTRAN compiler has been somewhat unsatisfactory. It is quite fast (within the limitations of the very slow input and output devices available) but generates many more incorrect object programs than it should. The CDC Software group in Palo Alto which is responsible for writing and maintaining the compiler has not released a corrected version, although several have been made at the CDC La Jolla Division. When compiler-generated object code errors cannot be removed by changing the source program, it is possible to use the compiler at the La Jolla plant. Hopefully, these troubles should end soon with the release by CDC of a mass store FORTRAN and operating

system. The new operating system should be a considerable improvement over the current one, since it includes provisions for a program library on the disc, a relocating loader that can search the disc for subroutines needed (those in the utility package, for example), and a load-and-go option for quick checking of new programs.

Several data acquisition systems have been written and are in routine use at General Atomic. The first system operates as a very simple 1024 channel time analyzer. The second (called the TMC Emulator) is a more sophisticated time analysis program with two separate banks of 1024 channels, and the third is an arbitrary time boundary analyzer (time boundaries corresponding to constant $\Delta E/E$ or constant ΔE may be chosen). All these programs are designed to operate using the El Dorado 5 nsec/channel analogue-to-digital converter. A chassis containing a dual ADC is currently being interfaced to the computer. This will accept the present TMC logic modules including a new 4096-channel pulse height module. This will permit us to perform time-of-flight and pulse height analysis simultaneously. This could be used for instance to refine the quality of our spectral data. Present use of the disc has been as a fast back-up storage - all the time spectra measured during a LINAC run are stored on the disc - since it takes about 10 minutes to punch a 1024-channel spectrum and only a few milliseconds to write it on the disc. This system will stop being effective as the data taking use of the computer increases. We will soon reach a point at which a good part of the computer time will be taken up by the extremely slow input/output devices.

An additional input device has been designed and is being built by the LINAC electronics group. This is a combination thumbwheel and pushbutton data entry device which will operate through the interrupt system to control simple functions such as display selection, resetting and printout without entering commands through the keyboard. This device should simplify computer use for data taking.

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AB INITIO CALCULATIONS OF PHONON DISPERSION CURVES

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APPENDIX A

AB INITIO CALCULATIONS OF PHONON DISPERSION CURVES

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1. INTRODUCTION

The calculation of phonon dispersion curves by means of the Born-Huang⁽¹⁾ theory of lattice dynamics has been carried out by many researchers. Generally these calculations have been in terms of force constants that are determined experimentally in one way or another. A favorite technique, and an effective one, is to fit the calculated dispersion curves to dispersion curves that have been determined from coherent one-phonon neutron scattering from single crystals. This method results in a force model which quite often reproduces other known data. In recent years it has become apparent that it is possible to calculate the phonon frequencies by solving, in effect, the Schrodinger equation for the crystal. In other words the calculations are done from first principles. The first such calculation was done for sodium some years ago. However, sodium is a particularly simple example due to the fact that the electrons in this metal have a spherical Fermi surface and the crystal has a simple structure. More complicated crystals are naturally much more difficult to treat and the results are not very satisfactory. Nevertheless, it is important to make such calculations in order to better understand the effects of the crystal potentials on the lattice dynamics of crystals.

We give here a general theory of lattice dynamical calculations in the harmonic approximation from first principles, reserving the numerical results for a later paper. The method involves finding the one-electron energies from a variational principle and then performing an expansion to second order in the ionic displacements. The corrections to the one-electron energies and wave functions due to ionic displacements are found by ordinary perturbation theory. In this manner

we find the second order contribution of the electrons to the ion energy. The theory is carried through with Slater exchange, but any exchange potential could be utilized. An expansion in normal coordinates leads one to an expression for the electronic contribution to the phonon energies. In Section 2 is presented a derivation of the pure Coulomb contribution for the interaction between the positive ions. Section 3 deals with the ground state energy of a distorted crystal, Section 4 covers the electronic ground state energy to second order in the ionic displacements and Section 7 presents the proof that the theory satisfies infinitesimal translational invariance.

2. ION-CORE - ION-CORE INTERACTION

In this section we derive the contribution to the dynamical matrix from the pure Coulomb repulsive interaction between the ion cores. The treatment here follows closely that given by M. Born and K. Huang.⁽¹⁾

The Coulomb part of the dynamical matrix is expressed in terms of the quantities:

$$\Phi_{\alpha\beta}^c \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \left. \frac{\partial^2 \Phi^c}{\partial u_{\alpha}(lk) \partial u_{\beta}(lk)} \right|_0,$$

by means of the expression

$$W_{\alpha\beta}^c \begin{pmatrix} q \\ kk' \end{pmatrix} = \frac{e^{iq \cdot (\underline{\chi}(k) - \underline{\chi}(k'))}}{\sqrt{M_k M_{k'}}} \sum_l \Phi_{\alpha\beta}^c \begin{pmatrix} ol \\ kk' \end{pmatrix} e^{-iq \cdot \underline{\chi}(l)}$$

where M_k is the mass of the k^{th} atom in a unit cell, $\underline{\chi}(k)$ its position vector in the cell, q is the wave-vector restricted to the first Brillouin zone, and $\underline{\chi}(l)$ a vector in the direct lattice. Here $\underline{u}(lk)$ is the small displacement of the atom (lk) from its equilibrium position. For the electrostatic potential energy of interaction we write

$$\Phi^c = \frac{1}{2} \sum_{lk} \sum_{lk'}' \frac{e_k e_{k'}}{|\underline{\chi}(lk) + \underline{u}(lk) - \underline{\chi}(lk') - \underline{u}(lk')|^3}$$

from which we obtain

$$\begin{aligned}
\Phi_{\alpha\beta}^c \begin{pmatrix} \ell \ell' \\ k k' \end{pmatrix} = & - e_k e_{k'} \left[3 \frac{(\chi_\alpha(\ell k) - \chi_\alpha(\ell' k') - \chi_\beta(\ell k) - \chi_\beta(\ell' k'))}{|\chi(\ell k) - \chi(\ell' k')|^5} \right. \\
& \left. - \delta_{\alpha\beta} \frac{1}{|\chi(\ell k) - \chi(\ell' k')|^3} \right] \\
& + e_k \delta_{kk'} \delta_{\ell\ell'} \sum_{\ell'' k''}' e_{k''} \left[3 \frac{(\chi_\alpha(\ell k) - \chi_\alpha(\ell'' k'')(\chi_\beta(\ell k) - \chi_\beta(\ell'' k''))}{|\chi(\ell k) - \chi(\ell'' k'')|^5} \right. \\
& \left. - \delta_{\alpha\beta} \frac{1}{|\chi(\ell k) - \chi(\ell'' k'')|^3} \right]
\end{aligned}$$

where e_k is the charge on the k^{th} atom in a unit cell, and the prime on the sums implies that the terms where the denominator vanish are excluded.

As is well-known the above expressions are difficult to evaluate numerically due to slow convergence of the sums over the direct lattice. It is necessary then to use the famous theta-function transformation due to Ewald. Note that

$$\left[\frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \frac{1}{|\chi - \chi(\ell' k')|} \right]_{\chi = \chi(k)} = \left[\frac{2}{\sqrt{\pi}} \frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \int_0^\infty d\rho \rho^{-1} |\chi - \chi(\ell' k')|^2 \rho^{-2} \right]_{\chi = \chi(k)}$$

Our dynamical matrix can then be expressed in this fashion

$$W_{\alpha\beta}^c \begin{pmatrix} q \\ kk' \end{pmatrix} = - (2\sqrt{\pi}) e_k e_{k'} (M_k M_{k'})^{-1/2} \exp \left(i \underline{q} \cdot (\chi(k) - \chi(k')) \right)$$

$$\sum_{\ell} e^{i \underline{q} \cdot \chi(\ell)} \left[\frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \int_0^\infty d\rho \rho^{-1} |\chi - \chi(\ell k')|^2 \rho^{-2} \right]_{\chi = \chi(k)}$$

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$$+ (2/\sqrt{\pi}) e_k M_k^{-1} \delta_{kk'} \sum_{\ell k''} e_{k''} \left[\frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \int_0^\infty d\rho \ell^{-|\chi - \chi(\ell k'')|^2 \rho^2} \right]_{\chi = \chi(k)}$$

At this point we make use of the fact that if a function, say $f(\chi)$ is periodic in χ , it can be expressed in a Fourier series

$$f(\chi) = \sum_{\underline{G}} g(\underline{G}) e^{i \underline{G} \cdot \chi}$$

with the coefficients $g(\underline{G})$ defined by

$$g(\underline{G}) = \frac{1}{\Omega_c} \int_{\Omega_c} d^3 \chi f(\chi) e^{-i \underline{G} \cdot \chi}$$

where $\underline{G}$ is a vector in the reciprocal lattice and Ω_c is the volume of a unit cell. Now the quantity

$$\frac{2}{\sqrt{\pi}} \sum_{\ell} \ell^{-|\chi - \chi(\ell k'')|^2 \rho^2}$$

is periodic in ℓ and hence can be written as a Fourier series with coefficients

$$g(\underline{G}) = \frac{1}{\Omega_c} \sum_{\ell} \int_{\Omega_c} d^3 \chi \frac{2}{\sqrt{\pi}} \ell^{-|\chi - \chi(\ell k'')|^2 \rho^2} e^{-i \underline{G} \cdot \chi}$$

We include here all values of ℓ in the realization that the terms which were previously excluded are equal except for a difference in sign and hence cause no difficulty. By making the substitution $\chi \rightarrow \chi - \chi(\ell)$, the integral can be written more transparently

$$g(\underline{G}) = \frac{1}{\Omega_c} \frac{2}{\sqrt{\pi}} \int_{\text{all space}} d^3 \underline{\chi} e^{-i \underline{G} \cdot \underline{\chi}} e^{-|\underline{\chi}(k'') - \underline{\chi}|^2 \rho^2}$$

or

$$g(\underline{G}) = \frac{2\pi}{\Omega_c} \rho^{-3} \exp(-\underline{G}^2/4\rho^2) e^{-i \underline{G} \cdot \underline{\chi}(k'')}$$

We have then the relation

$$\frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-|\underline{\chi} - \underline{\chi}(\ell k'')|^2 \rho^2} = \frac{2\pi}{\Omega_c} \rho^{-3} \sum_{\underline{G}} e^{-\frac{\underline{G}^2}{4\rho^2}} e^{i \underline{G} \cdot (\underline{\chi} - \underline{\chi}(k''))}$$

By means of the very same analysis,

$$\begin{aligned} \frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-i \underline{q} \cdot (\underline{\chi} - \underline{\chi}(\ell k'))} e^{-|\underline{\chi} - \underline{\chi}(\ell k')|^2 \rho^2} \\ = \frac{2\pi}{\Omega_c} \rho^{-3} \sum_{\underline{G}} e^{i \underline{G} \cdot (\underline{\chi} - \underline{\chi}(k'))} e^{-\frac{|\underline{q} + \underline{G}|^2}{4\rho^2}} \end{aligned}$$

To use the above results to advantage in the expression for our dynamical matrix we split the integral over ρ into two parts:

$$\int_0^\infty d\rho \equiv \int_0^R d\rho + \int_R^\infty d\rho$$

with the number R being called the "splitting" parameter. Thus we have

$$W_{\alpha\beta} \left(\begin{smallmatrix} q \\ k k' \end{smallmatrix} \right) = - \frac{e_k e_{k'}}{(M_k M_{k'})^{1/2}} e^{i \underline{q} \cdot \underline{\chi}(k)} \frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \left[\int_R^\infty d\rho \frac{2}{\sqrt{\pi}} \right]$$

$$\begin{aligned}
& \sum_{\ell} e^{-i \underline{q} \cdot \underline{\chi}(\ell k')} e^{-|\underline{\chi} - \underline{\chi}(ek')|^2 \rho^2} + \int_0^R d\rho \frac{2\pi}{\Omega_c} \\
& \sum_{\underline{G}} \rho^{-3} e^{i \underline{G} \cdot (\underline{\chi} - \underline{\chi}(k'))} e^{-|\underline{q} + \underline{G}|^2 \rho^2 / 4} e^{-i \underline{q} \cdot \underline{\chi}} \left. \right\}_{\underline{\chi} = \underline{\chi}(k)} \\
& + \frac{e_k \delta_{kk'}}{M_k} \sum_{k''} e_{k''} \left\{ \frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \left[\int_R^\infty d\rho \frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-|\underline{\chi} - \underline{\chi}(ek'')|^2 \rho^2} \right. \right. \\
& \left. \left. + \int_0^R d\rho \frac{2\pi}{\Omega_c} \rho^{-3} \sum_{\underline{G}} e^{-\rho^2 \underline{G}^2 / 4} e^{i \underline{G} \cdot (\underline{\chi} - \underline{\chi}(k''))} \right] \right\}_{\underline{\chi} = \underline{\chi}(k)}
\end{aligned}$$

The very last term in the above expression becomes upon performing the indicated integration

$$\begin{aligned}
& \frac{2\pi}{\Omega_c} \frac{e_k \delta_{kk'}}{M_k} \sum_{k''} e_{k''} \sum_{\underline{G}} \left\{ \frac{\partial^2}{\partial \chi_\alpha \partial \chi_\beta} \left(e^{i \underline{G} \cdot (\underline{\chi} - \underline{\chi}(k''))} \int_0^R d\rho \rho^{-3} e^{-\frac{\underline{G}^2}{4\rho^2}} \right) \right\}_{\underline{\chi} = \underline{\chi}(k)} \\
& = - \frac{e_k \delta_{kk'}}{M_k} \sum_{k''} e_{k''} \left[\frac{4\pi}{\Omega_c} \sum_{\underline{G}} \frac{G_\alpha G_\beta}{|\underline{G}|^2} e^{-\underline{G}^2 / 4R^2} e^{i \underline{G} \cdot (\underline{\chi}(k) - \underline{\chi}(k''))} \right]
\end{aligned}$$

Note the indeterminate form of the summand when $\underline{G} = 0$. This term does not occur however if the total charge of the ions in a unit cell of the crystal vanish, i. e.,

$$\sum_{k''} e_{k''} = 0,$$

which indeed does occur in an ionic crystal, for example. In our particular

case of a Coulomb lattice of positive ions, this term does not vanish. Nevertheless, it will always be cancelled by an equal and opposite contribution from the electrons, since our real insulator does indeed have charge neutrality. This can also be seen by calculating the contribution to the lattice dynamics from an interaction between our positive ion lattice and a uniform compensating negative background.

By performing the remaining integrations, our Coulomb contribution to the dynamical matrix is then

$$\begin{aligned}
W_{\alpha\beta}^c \left(\begin{matrix} q \\ k k' \end{matrix} \right) = & \frac{e_k e_{k'}}{(M_k M_{k'})^{1/2}} \left[\frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-i \underline{q} \cdot \underline{P}} \left\{ P_{\alpha} P_{\beta} \left(2 R^3 P^{-2} e^{-P^2 R^2} \right. \right. \right. \\
& + \left. \left. 3 R P^{-4} e^{P^2 R^2} + (3\sqrt{\pi}/2P^5) \text{Erfc}(RP) \right) - \delta_{\alpha\beta} \left(R P^2 e^{-P^2 R^2} \right. \right. \\
& + \left. \left. (\sqrt{\pi}/2P^3) \text{Erfc}(RP) \right) \right\} - \frac{4\pi}{\Omega_c} \sum_{\underline{G}} \frac{(q_{\alpha} + G_{\alpha})(q_{\beta} + G_{\beta})}{|\underline{q} + \underline{G}|^2} e^{-|\underline{q} + \underline{G}|^2/4R^2} \\
& e^{+i \underline{G} \cdot (\underline{\chi}(k') - \underline{\chi}(k))} \left. \right] + \frac{e_k \delta_{k k'}}{M_k} \sum_{k''} e_{k''} \\
& \left[\frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-i \underline{q} \cdot \underline{L}} \left\{ L_{\alpha} L_{\beta} \left(2 R^3 L^{-2} e^{-L^2 R^2} + 3 R L^{-4} e^{-L^2 R^2} \right. \right. \right. \\
& + \left. \left. (3\sqrt{\pi}/2L^5) \text{Erfc}(RL) \right) - \delta_{\alpha\beta} \left(R L^{-2} e^{-L^2 R^2} + (\sqrt{\pi}/2L^3) \text{Erfc}(RL) \right) \right\}
\end{aligned}$$

$$- \frac{4\pi}{\Omega_c} \sum_{\underline{G}}' \frac{G_\alpha G_\beta}{|\underline{G}|^2} e^{-\underline{G}^2/4R^2} e^{i \underline{G} \cdot (\underline{\chi}(k'') - \underline{\chi}(k))} \Bigg]$$

where $\underline{P} \equiv \underline{\chi}(\ell k') - \underline{\chi}(k)$, $P \equiv |\underline{P}|$, $\underline{L} \equiv \underline{\chi}(\ell k'') - \underline{\chi}(k)$, $L \equiv |\underline{L}|$,
and $\text{Erfc}(x) = 1 - \text{Erf}(x)$. The prime on the summations implying,
as before, that the terms with a vanishing denominator are not to be
included.

3. THE GROUND STATE ENERGY OF A DISTORTED CRYSTAL

In this section we carry out a formal expansion of the ground state energy of the valence electrons in an arbitrary non-primitive crystal to second order in the displacements of the ion cores from their equilibrium positions.

The Hamiltonian for the system of n valence electrons in a crystal can be written in the form

$$H = \sum_i^n \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V(\underline{r}_i) \right\} + \frac{1}{2} e^2 \sum_{ij}^n \frac{1}{r_{ij}} \quad (3.1)$$

The summation variables i and j run over the valence electrons in the crystal, which are assumed to be the only dynamic electrons in the crystal. The core electrons on each atom are assumed to move rigidly with the nucleus, and with the nucleus give rise to a bare electron-ion potential $V(\underline{r})$. If we denote by $U_k(\underline{r})$ the potential energy due to the ion core of the k^{th} kind of atom, the potential $V(\underline{r})$ can be written as

$$V(\underline{r}) = \sum_{\ell k} U_k(\underline{r} - \underline{R}(\ell k)) \quad (3.2)$$

where $\underline{R}(\ell k)$ is the instantaneous position of the k^{th} nucleus in the ℓ^{th} unit cell of the crystal.

In the Hartree-Fock approximation the wave function for the ground state of the Hamiltonian (3.1) is written as a Slater determinant of one electron wave functions

$$\psi_0 = (n!)^{-1/2} \begin{vmatrix} \varphi_1(\underline{x}_1) & \varphi_1(\underline{x}_2) & \dots & \varphi_1(\underline{x}_n) \\ \varphi_2(\underline{x}_1) & \varphi_2(\underline{x}_2) & \dots & \varphi_2(\underline{x}_n) \\ \dots & \dots & \dots & \dots \\ \varphi_n(\underline{x}_1) & \varphi_n(\underline{x}_2) & \dots & \varphi_n(\underline{x}_n) \end{vmatrix} \quad (3.3)$$

where $\underline{x}_i$ denotes the space and spin coordinates of the electron i . The functions $\{\varphi_i(\underline{x}_j)\}$ are assumed to be orthonormal

$$\int \varphi_i^*(\underline{x}) \varphi_j(\underline{x}) d\underline{x} = \delta_{ij} \quad (3.4)$$

The expectation value of the Hamiltonian (3.1) with respect to the wave function (3.3) is an estimate of the ground state energy of the system of valence electrons,

$$\begin{aligned} \epsilon_0 = & \sum_{i=1}^n \int \varphi_i^*(\underline{x}) H_1(\underline{x}) \varphi_i(\underline{x}) d\underline{x} + \\ & + \frac{e^2}{2} \sum_{i=1}^n \sum_{j=1}^n \int \frac{|\varphi_i(\underline{x}_1)|^2 |\varphi_j(\underline{x}_2)|^2}{r_{12}} d\underline{x}_1 d\underline{x}_2 \\ & - \frac{e^2}{2} \sum_{i=1}^n \sum_{j=1}^n \int \frac{\varphi_i^*(\underline{x}_1) \varphi_j^*(\underline{x}_2) \varphi_j(\underline{x}_1) \varphi_i(\underline{x}_2)}{r_{12}} d\underline{x}_1 d\underline{x}_2 \end{aligned} \quad (3.5)$$

where $H_1(\underline{x})$ is the one electron Hamiltonian

$$H_1(\underline{x}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{x}). \quad (3.6)$$

The best one electron wave functions $\{\varphi_i(\underline{x}_j)\}$ are those which minimize ϵ_0 subject to the constraint (3.4). From Eq. (3.5) it follows that these wave functions are the solutions of the coupled set of equations

$$\begin{aligned}
H_1 \varphi_i(\underline{x}_1) + e^2 \sum_{j=1}^n \int \frac{|\varphi_j(\underline{x}_2)|^2}{r_{12}} d\underline{t}_2 \varphi_i(\underline{x}_1) \\
- e^2 \sum_{j=1}^n \int \frac{\varphi_j^*(\underline{x}_2) \varphi_i(\underline{x}_2)}{r_{12}} d\underline{t}_2 \varphi_j(\underline{x}_1) = E_i \varphi_i(\underline{x}_1)
\end{aligned} \quad (3.7)$$

Multiplying both sides of this equation by $\varphi_i^*(\underline{x}_1)$, integrating over $\underline{x}_1$, and summing over i , it follows that

$$\begin{aligned}
\sum_{i=1}^n \int \varphi_i^*(\underline{x}) H_1(\underline{x}) \varphi_i(\underline{x}) d\underline{t} = \sum_{i=1}^n E_i - \\
- e^2 \sum_{i=1}^n \sum_{j=1}^n \int \frac{|\varphi_i(\underline{x}_1)|^2 |\varphi_j(\underline{x}_2)|^2}{r_{12}} d\underline{t}_1 d\underline{t}_2 + \\
+ e^2 \sum_{i=1}^n \sum_{j=1}^n \int \frac{\varphi_i^*(\underline{x}_1) \varphi_j^*(\underline{x}_2) \varphi_i(\underline{x}_2) \varphi_j(\underline{x}_1)}{r_{12}} d\underline{t}_1 d\underline{t}_2
\end{aligned} \quad (3.8)$$

By the use of this result we can rewrite the ground state energy, Eq. (3.5), in the form

$$\begin{aligned}
\epsilon_0 = \sum_{i=1}^n E_i - \frac{e^2}{2} \sum_{i=1}^n \sum_{j=1}^n \int \frac{|\varphi_i(\underline{x}_1)|^2 |\varphi_j(\underline{x}_2)|^2}{r_{12}} d\underline{t}_1 d\underline{t}_2 \\
+ \frac{e^2}{2} \sum_{i=1}^n \sum_{j=1}^n \int \frac{\varphi_i^*(\underline{x}_1) \varphi_j^*(\underline{x}_2) \varphi_i(\underline{x}_2) \varphi_j(\underline{x}_1)}{r_{12}} d\underline{t}_1 d\underline{t}_2
\end{aligned} \quad (3.9)$$

We have remarked previously that the variable $\underline{x}_i$ ($i = 1, 2, \dots, n$) consists of two parts: a spatial position coordinate r_j and a spin variable ζ_j . The wave function (3.3) is the only combination of the $\{\varphi_i(\underline{x}_j)\}$ which

is antisymmetric in the spatial and spin variables. In this paper we will write the one electron wave function $\varphi_i(\chi_j)$ as the product of a function of the space coordinates along $\psi_i(\underline{r}_j)$ times a function of the spin coordinates alone $\eta_i(\zeta_j)$. We assume that $\eta_i(\zeta_j)$ is an eigenfunction of the Z-component of the spin operator σ_Z , so that ζ_j takes on the two values $\zeta_j = +1$ and $\zeta_j = -1$, corresponding to the eigenvalues $+\hbar/2$ and $-\hbar/2$, respectively. In general the wave function (3.3) is not the only antisymmetric combination of the coordinate wave functions $\{\psi_i(\underline{r}_j)\}$ because it may be possible to assign spin functions to the $\{\psi_i(\underline{r}_j)\}$ in more than one way. The Hamiltonian (3.1) is independent of spin, and its ground state for any of the non-magnetic crystals for which the theory developed in this paper is valid is nondegenerate. A satisfactory wave function for this situation is one in which the $\{\psi_i(\underline{r}_j)\}$ are equal in pairs

$$\psi_1 = \psi_2, \psi_3 = \psi_4, \dots, \psi_{n-1} = \psi_n, \quad (3.10)$$

and the spins of the members of equal pairs are opposite.

The preceding considerations suggest that because there are only $n/2$ different coordinate wave functions $\{\psi_i(\underline{r}_j)\}$ a change of notation which takes explicit account of this fact will be useful. Let us denote by μ ($=1, 2, \dots, n/2$) all of the quantum numbers which are required to specify the spatial part of the wave function $\varphi_i(\chi_j)$, and by m_μ . The spin quantum number associated with the state μ m_μ takes on the values $+1$ or -1 , corresponding to the eigenvalues $+\hbar/2$ and $-\hbar/2$ of the operator σ_Z . The wave function $\varphi_i(\chi_j)$ can therefore be rewritten as

$$\varphi_i(\chi_j) \rightarrow \varphi_{\mu j m_\mu}(\chi_j) = \psi_\mu(\underline{r}_j) \eta_{m_\mu}(\zeta_j). \quad (3.11)$$

Summation over the index i is therefore equivalent to the double summation

$$\sum_{i=1}^n = \sum_{\mu=1}^{n/2} \sum_{m_\mu = -1}^{+1}. \quad (3.12)$$

In the present case a convenient representation of $\eta_{m_\mu}(\zeta_j)$ is

$$\eta_{m_\mu}(\zeta_j) = \delta(m_\mu, \zeta_j) = \begin{cases} 1 & \text{if } m_\mu = \zeta_j \\ 0 & \text{if } m_\mu \neq \zeta_j \end{cases} \quad (3.13)$$

Integration over the variable χ_i in Eqs. (3.5) and (3.7)-(3.9) denotes an integration over the coordinate $\tilde{r}_i$ and a summation over the two values of the spin variable ζ_i ,

$$\int d\tilde{t}_i = \sum_{\zeta_i = -1}^{+1} \int d^3 \tilde{r}_i \quad (3.14)$$

From Eq. (3.13) it follows that the operators $\{\eta_{m_\mu}(\zeta_j)\}$ are orthonormal

$$\sum_{\zeta_j} \eta_{m_\mu}(\zeta_j) \eta_{m_{\mu'}}(\zeta_j) = \delta(m_\mu, m_{\mu'}) \quad (3.15)$$

It is convenient to introduce the number densities of electrons with spin up and with spin down,

$$\begin{aligned} \rho_{+}(\tilde{r}) &= \sum_{\mu}^{n/2} \sum_{m_\mu = -1}^{+1} |\psi_{\mu}(\tilde{r}) \eta_{m_\mu}(+)|^2 \\ &= \sum_{\mu}^{n/2} |\psi_{\mu}(\tilde{r})|^2 \end{aligned} \quad (3.16a)$$

$$\begin{aligned}
\rho_{-}(\underline{r}) &= \sum_{\mu}^{n/2} \sum_{m_{\mu}=-1}^{+1} |\psi_{\mu}(\underline{r}) \eta_{m_{\mu}}(-)|^2 \\
&= \sum_{\mu}^{n/2} |\psi_{\mu}(\underline{r})|^2 = \rho_{+}(\underline{r}) .
\end{aligned} \tag{3.16b}$$

The total number density of electrons $\rho(\underline{r}) = \rho_{+}(\underline{r}) + \rho_{-}(\underline{r})$ can be written conveniently as

$$\rho(\underline{r}) = \sum_{\mu} \theta_{\mu} |\psi_{\mu}(\underline{r})|^2 , \tag{3.17}$$

where $\theta_{\mu} = 2$ if μ labels an occupied state (i. e., if $\mu = 1, 2, \dots, n/2$), and $\theta_{\mu} = 0$ if μ labels an unoccupied state (i. e., if $\mu > n/2$).

It is also convenient to introduce the functions

$$\begin{aligned}
\rho(\underline{r}_1 \zeta_1; \underline{r}_2 \zeta_2) &= \sum_{\mu} \sum_{m_{\mu}} \varphi_{\mu; m_{\mu}}(\underline{r}_1) \varphi_{\mu; m_{\mu}}^{*}(\underline{r}_2) \\
&= \sum_{\mu} \psi_{\mu}(\underline{r}_1) \psi_{\mu}^{*}(\underline{r}_2) \sum_{m_{\mu}} \eta_{m_{\mu}}(\zeta_1) \eta_{m_{\mu}}(\zeta_2).
\end{aligned} \tag{3.18}$$

Recalling Eqs. (3.13) we obtain the results that

$$\begin{aligned}
\rho(\underline{r}_1 +; \underline{r}_2 +) &= \rho(\underline{r}_1 -; \underline{r}_2 -) = \sum_{\mu}^{n/2} \psi_{\mu}(\underline{r}_1) \psi_{\mu}^{*}(\underline{r}_2) \\
&= \frac{1}{2} \sum_{\mu} \theta_{\mu} \psi_{\mu}(\underline{r}_1) \psi_{\mu}^{*}(\underline{r}_2) \equiv \frac{1}{2} \rho(\underline{r}_1, \underline{r}_2)
\end{aligned} \tag{3.19}$$

$$\rho(\underline{r}_1 + ; \underline{r}_2 -) = \rho(\underline{r}_1 - ; \underline{r}_2 +) = 0 \quad (3.20)$$

The factor of $1/2$ on the right hand side of Eq. (3.19) has been introduced so that $\rho(\underline{r}_1, \underline{r}_2) \rightarrow \rho(\underline{r}_1)$ as $\underline{r}_2 \rightarrow \underline{r}_1$.

Finally, we note that with the change of notation implied by Eq. (3.11), the energy eigenvalue E_i should be rewritten as $E_{\underline{\mu}; m_{\underline{\mu}}}$. However, because the Hamiltonian (3.1) is independent of spin, we must have that

$$E_{\underline{\mu}; m_{\underline{\mu}}} = E_{\underline{\mu}}, \quad (3.21)$$

independent of $m_{\underline{\mu}}$.

The Hartree-Fock equations for the wave functions $\{\psi_{\underline{\mu}}(\underline{r})\}$ can now be written compactly as

$$\left\{ H_1(\underline{r}_1) + e^2 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_2)}{r_{12}} \right\} \psi_{\underline{\mu}}(\underline{r}_1) - \frac{e^2}{2} \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1, \underline{r}_2)}{r_{12}} \psi_{\underline{\mu}}(\underline{r}_2) = E_{\underline{\mu}} \psi_{\underline{\mu}}(\underline{r}_1) \quad (3.22)$$

Because the $\{\psi_{\underline{\mu}}(\underline{r})\}$ are the eigenfunctions of a Hermitean operator, we can assume them to be orthonormal

$$\int d^3 \underline{r} \psi_{\underline{\mu}}^*(\underline{r}) \psi_{\underline{\nu}}(\underline{r}) = \delta_{\underline{\mu}\underline{\nu}} \quad (3.23)$$

The expression for the ground state energy ϵ_0 given by Eq. (3.9) can also be rewritten compactly as

$$\begin{aligned} \epsilon_0 = & \sum_{\underline{\mu}} \theta_{\underline{\mu}} \int d^3 \underline{r}_1 \psi_{\underline{\mu}}^*(\underline{r}_1) H_1(\underline{r}_1) \psi_{\underline{\mu}}(\underline{r}_1) + \\ & + \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1) \rho(\underline{r}_2)}{r_{12}} - \\ & - \frac{e^2}{4} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1, \underline{r}_2) \rho(\underline{r}_2, \underline{r}_1)}{r_{12}} \end{aligned} \quad (3.24)$$

$$\begin{aligned}
&= \sum_{\mu} \theta_{\mu} E_{\mu} - \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1) \rho(\underline{r}_2)}{r_{12}} + \\
&+ \frac{e^2}{4} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1, \underline{r}_2) \rho(\underline{r}_2, \underline{r}_1)}{r_{12}} \quad (3.25)
\end{aligned}$$

Because of the nonlocal character of the exchange term in the Hamiltonian defined by Eq. (3.22). The problem of solving the coupled integro-differential equations (3.22) for the one electron wave functions in a crystal is a very difficult one, so that in many calculations of crystal properties on the basis of The Hartree-Fock method, a simple, local approximation for the exchange term, first proposed by Slater,⁽³⁾ has been used. This form for the exchange potential is obtained if it is assumed that the exchange potential in a crystal with a given charge density $-e\rho(\underline{r})$ is the same as in a free electron gas of the same density, and is given by

$$\begin{aligned}
V_{\text{ex}}(\underline{r}) &= -\lambda e^2 \left(\frac{3}{4\pi} \rho_+(\underline{r}) \right)^{1/3} \\
&= -\lambda e^2 \left(\frac{3}{8\pi} \rho(\underline{r}) \right)^{1/3} \quad (3.26)
\end{aligned}$$

In Slater's derivation of the form of the exchange potential given by Eq. (3.26) the multiplicative constant λ equals 3. More recently Gaspar and Kohn and Sham have given an alternative derivation of a free electron approximation to the exchange potential which is based on a variational principle for the electronic ground state energy and yields Eq. (3.26), but with λ equal to 2. Other authors have used λ as an adjustable parameter whose value is determined so as to make calculated band structures agree as closely as possible with experimental results. In what follows we will develop the theory on the basis of the form of $V_{\text{ex}}(\underline{r})$ given by E . (3.25) without committing ourselves to a particular value of λ until the numerical work.

The Hartree-Fock equations (3.22) now take the form

$$\left\{ H_1(\underline{r}_1) + e^2 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_2)}{r_{12}} - \lambda e^2 \left(\frac{3}{8\pi} \right)^{1/3} \rho^{1/3}(\underline{r}_1) \right\} \psi_\mu(\underline{r}_1) = E_\mu \psi_\mu(\underline{r}_1). \quad (3.27)$$

Just as Eq. (3.22) is the Euler equation for the function $\psi_\mu(\underline{r})$ which minimizes the energy functional (3.24), Eq. (3.27) is the Euler equation for the function $\psi_\mu(\underline{r})$ which minimizes the energy functional

$$\begin{aligned} \varepsilon_0 = & \sum_\mu \int d^3 \underline{r}_1 \psi_\mu^*(\underline{r}_1) H_1(\underline{r}_1) \psi_\mu(\underline{r}_1) + \\ & + \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1) \rho(\underline{r}_2)}{r_{12}} - \frac{3}{4} \lambda e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r}_1 \rho^{4/3}(\underline{r}_1) \end{aligned} \quad (3.28)$$

Combining Eqs. (3.27) and (3.28) we obtain an alternative expression for the ground state energy of our electronic system,

$$\begin{aligned} \varepsilon_0 = & \sum_\mu \int d^3 \underline{r}_1 \psi_\mu^*(\underline{r}_1) E_\mu \psi_\mu(\underline{r}_1) - \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho(\underline{r}_1) \rho(\underline{r}_2)}{r_{12}} + \\ & + \frac{1}{4} \lambda e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r}_1 \rho^{4/3}(\underline{r}_1), \end{aligned} \quad (3.29)$$

when the one electron wave functions $\{\psi_\mu(\underline{r})\}$ and energies $\{E_\mu\}$ which enter into this expression are solutions of Eqs. (3.27).

Equations (3.27) and (3.29) are the starting points for our calculation of the phonon dispersion curves of diamond.

4. ELECTRONIC GROUND STATE ENERGY TO SECOND ORDER IN THE NUCLEAR DISPLACEMENTS

If the nuclear positions in the distorted crystal are given by

$$\underline{R}(\ell k) = \underline{\chi}(\ell k) + \underline{U}(\ell k) , \quad (4.1)$$

where $\underline{\chi}(\ell k)$ is the position vector of the equilibrium position of the k^{th} atom in the ℓ^{th} unit cell, and $\underline{U}(\ell k)$ is the displacement of the nucleus (ℓk) from this position, the bare electron-ion potential $V(\underline{r})$ given by Eq. (3.2) can be expanded in powers of the nuclear displacements according to

$$V(\underline{r}) = V^{(0)}(\underline{r}) + V^{(1)}(\underline{r}) + V^{(2)}(\underline{r}) + \dots \quad (4.2)$$

where

$$V^{(0)}(\underline{r}) = \sum_{\ell k} U_k(\underline{r} - \underline{\chi}(\ell k)) \quad (4.3a)$$

$$V^{(1)}(\underline{r}) = - \sum_{\ell k \alpha} U_{\alpha}(\ell k) \frac{\partial}{\partial \chi_{\alpha}} U_k(\underline{r} - \underline{\chi}(\ell k)) \quad (4.3b)$$

$$V^{(2)}(\underline{r}) = \frac{1}{2} \sum_{\ell k \alpha \beta} U_{\alpha}(\ell k) U_{\beta}(\ell k) \frac{\partial^2}{\partial \chi_{\alpha} \partial \chi_{\beta}} U_k(\underline{r} - \underline{\chi}(\ell k)). \quad (4.3c)$$

Here and in all that follows a superscript attached to a quantity gives the order in the nuclear displacements to which that quantity is proportional.

If we treat $V^{(1)}(\underline{r})$ and $V^{(2)}(\underline{r})$ as perturbations on the bare electron-ion potential given $V^{(0)}(\underline{r})$, the one-electron wave function $\psi_{\mu}(\underline{r})$ must also be expanded in powers of the nuclear displacements:

$$\psi_{\mu}(\underline{r}) = \psi_{\mu}^{(0)}(\underline{r}) + \psi_{\mu}^{(1)}(\underline{r}) + \psi_{\mu}^{(2)}(\underline{r}) + \dots \quad (4.4)$$

It follows from Eqs. (3.17) and (4.4) that the number density of electrons can also be expanded in powers of the nuclear displacements:

$$\rho(\underline{r}) = \rho^{(0)}(\underline{r}) + \rho^{(1)}(\underline{r}) + \rho^{(2)}(\underline{r}) + \dots \quad (4.5)$$

where

$$\rho^{(0)}(\underline{r}) = \sum_{\mu} \theta_{\mu} |\psi_{\mu}^{(0)}(\underline{r})|^2 \quad (4.6a)$$

$$\rho^{(1)}(\underline{r}) = \sum_{\mu} \theta_{\mu} \left[\psi_{\mu}^{(0)*}(\underline{r}) \psi_{\mu}^{(1)}(\underline{r}) + \psi_{\mu}^{(1)*}(\underline{r}) \psi_{\mu}^{(0)}(\underline{r}) \right] \quad (4.6b)$$

$$\begin{aligned} \rho^{(2)}(\underline{r}) = \sum_{\mu} \theta_{\mu} \left[\psi_{\mu}^{(0)*}(\underline{r}) \psi_{\mu}^{(2)}(\underline{r}) + \psi_{\mu}^{(1)*}(\underline{r}) \psi_{\mu}^{(1)}(\underline{r}) + \right. \\ \left. + \psi_{\mu}^{(2)*}(\underline{r}) \psi_{\mu}^{(0)}(\underline{r}) \right]. \end{aligned} \quad (4.6c)$$

Finally, the one electron energies can be expanded in powers of the nuclear displacements:

$$E_{\mu} = E_{\mu}^{(0)} + E_{\mu}^{(1)} + E_{\mu}^{(2)} + \dots \quad (4.7)$$

If we substitute Eqs. (4.5) and (4.7), we see that the total ground state energy of the electronic system can be expanded in powers of the nuclear displacements:

$$\epsilon_o = \epsilon_o^{(0)} + \epsilon_o^{(1)} + \epsilon_o^{(2)} + \dots \quad (4.8)$$

where

$$\begin{aligned} \epsilon_o^{(0)} = & \sum_{\mu} \theta_{\mu} E_{\mu}^{(0)} - \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho^{(0)}(\underline{r}_1) \rho^{(0)}(\underline{r}_2)}{r_{12}} + \\ & + \frac{1}{4} \lambda e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \left[\rho^{(0)}(\underline{r}) \right]^{4/3} \end{aligned} \quad (4.9a)$$

$$\begin{aligned} \epsilon_o^{(1)} = & \sum_{\mu} \theta_{\mu} E_{\mu}^{(1)} - e^2 \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho^{(0)}(\underline{r}_1) \rho^{(1)}(\underline{r}_2)}{r_{12}} + \\ & + \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \rho^{(1)}(\underline{r}) \left[\rho^{(0)}(\underline{r}) \right]^{1/3} \end{aligned} \quad (4.9b)$$

$$\begin{aligned} \epsilon_o^{(2)} = & \sum_{\mu} \theta_{\mu} E_{\mu}^{(2)} - \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{2\rho^{(0)}(\underline{r}_1)\rho^{(2)}(\underline{r}_2) + \rho^{(1)}(\underline{r}_1)\rho^{(1)}(\underline{r}_2)}{r_{12}} + \\ & + \frac{\lambda}{4} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \int \frac{4}{3} \rho^{(2)}(\underline{r}) \left[\rho^{(0)}(\underline{r}) \right]^{1/3} + \frac{2}{9} \frac{\left[\rho^{(1)}(\underline{r}) \right]^2}{\left[\rho^{(0)}(\underline{r}) \right]^{2/3}} \dots \end{aligned} \quad (4.9c)$$

These expressions can be simplified if we make use of the Hartree-Fock equations (3.27).

If we rewrite Eq. (3.27) as

$$H\psi_{\mu}(\underline{r}) = E_{\mu}\psi_{\mu}(\underline{r}) , \quad (4.10)$$

The one-electron Hamiltonian H can be expanded in powers of the nuclear displacements when we substitute into the left hand side of Eq. (3.27).

The expansions given by Eqs. (4.2) and (4.5):

$$H = H^{(0)} + H^{(1)} + H^{(2)} + \dots \quad (4.11)$$

where

$$H^{(0)} = -\frac{\hbar^2}{2m} \nabla_1^2 + V^{(0)}(\underline{r}_1) + e^2 \int d^3 \underline{r}_2 \frac{\rho^{(0)}(\underline{r}_2)}{r_{12}} - \lambda e^2 \left(\frac{3}{8\pi} \right)^{1/3} [\rho^{(0)}(\underline{r}_1)]^{1/3} \quad (4.12a)$$

$$H^{(1)} = V^{(1)}(\underline{r}_1) + e^2 \int d^3 \underline{r}_2 \frac{\rho^{(1)}(\underline{r}_2)}{r_{12}} - \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \frac{\rho^{(1)}(\underline{r}_1)}{[\rho^{(0)}(\underline{r}_1)]^{2/3}} \quad (4.12b)$$

$$H^{(2)} = V^{(2)}(\underline{r}_1) + e^2 \int d^3 \underline{r}_2 \frac{\rho^{(2)}(\underline{r}_2)}{r_{12}} - \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \left\{ \frac{\rho^{(2)}(\underline{r}_1)}{[\rho^{(0)}(\underline{r}_1)]^{2/3}} - \frac{1}{3} \frac{[\rho^{(1)}(\underline{r}_1)]^2}{[\rho^{(0)}(\underline{r}_1)]^{5/3}} \right\} \quad (4.12c)$$

In all that follows we assume that the eigenfunctions $\{\psi_{\mu}^{(0)}(\underline{r})\}$ and eigenvalues $\{E_{\mu}^{(0)}\}$ of the zero order Hamiltonian $H^{(0)}$ describing the static, periodic crystal are known. A straightforward application of perturbation theory now yields the results that

$$E_{\mu}^{(1)} = \langle \mu | H^{(1)} | \mu \rangle \quad (4.13a)$$

$$E_{\mu}^{(2)} = \langle \mu | H^{(2)} | \mu \rangle + \sum_{\nu} \frac{|\langle \mu | H^{(1)} | \nu \rangle|^2}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \quad (4.13b)$$

$$\psi_{\mu}^{(1)}(\underline{r}) = \sum_{\nu} \frac{\langle \nu | H^{(1)} | \mu \rangle}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \psi_{\nu}^{(0)}(\underline{r}) \quad (4.13c)$$

where to simplify the notation we have denoted the one electron wave function $\psi_{\mu}^{(0)}(\underline{r})$ by $|\mu\rangle$ in expressions for matrix elements. Combining Eqs. (4.6b) and (4.13c) we find that

$$\begin{aligned}
\rho^{(1)}(\underline{r}) &= \sum_{\mu} \theta_{\mu} \sum_{\nu}^1 \frac{\langle \nu | H^{(1)} | \mu \rangle}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \psi_{\mu}^{(0)*}(\underline{r}) \psi_{\nu}^{(0)}(\underline{r}) + \\
&+ \sum_{\mu} \theta_{\mu} \sum_{\nu}^1 \frac{\langle \nu | H^{(1)} | \mu \rangle^*}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \psi_{\mu}^{(0)}(\underline{r}) \psi_{\nu}^{(0)*}(\underline{r}) \\
&= \sum_{\mu\nu}^1 \frac{\theta_{\mu} - \theta_{\nu}}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \langle \nu | H^{(1)} | \mu \rangle \psi_{\mu}^{(0)*}(\underline{r}) \psi_{\nu}^{(0)}(\underline{r}) . \quad (4.14)
\end{aligned}$$

Substituting Eqs. (4.13a) and (3.17) into Eq. (4.9b), we can write the first order contribution to the ground state energy of the electronic system as

$$\begin{aligned}
\epsilon_o^{(1)} &= \sum_{\mu} \theta_{\mu} \left\{ \langle \mu | H^{(1)} | \mu \rangle \right. \\
&- e^2 \int d^3 \underline{r}_2 \rho^{(1)}(\underline{r}_2) \int d^3 \underline{r}_1 \psi_{\mu}^{(0)*}(\underline{r}_1) \frac{1}{r_{12}} \psi_{\mu}^{(0)}(\underline{r}_1) + \\
&\left. + \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \frac{\rho^{(1)}(\underline{r})}{[\rho^{(0)}(\underline{r})]^{2/3}} \psi_{\mu}^{(0)*}(\underline{r}) \psi_{\mu}^{(0)}(\underline{r}) \right\} \quad (4.15)
\end{aligned}$$

Combining Eqs. (4.12b) and (4.15) we obtain finally

$$\begin{aligned}
\epsilon_o^{(1)} &= \sum_{\mu} \theta_{\mu} \langle \mu | V^{(1)} | \mu \rangle \\
&= \int d^3 \underline{r} \rho^{(0)}(\underline{r}) V^{(1)}(\underline{r}) . \quad (4.16)
\end{aligned}$$

In a similar fashion we can simplify the expression (4.9c) for the second order contribution to the ground state energy of the electronic system. Combining Eqs. (4.9c) and (4.13b) we find that

$$\begin{aligned} \epsilon_o^{(2)} = \sum_{\mu} \theta_{\mu} \left\{ \langle \mu | H^{(2)} | \mu \rangle + \sum_{\nu}^1 \frac{|\langle \mu | H^{(1)} | \nu \rangle|^2}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \right\} \\ - \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{2 \rho^{(0)}(\underline{r}_1) \rho^{(2)}(\underline{r}_2) + \rho^{(1)}(\underline{r}_1) \rho^{(1)}(\underline{r}_2)}{r_{12}} + \\ + \frac{\lambda}{4} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \left\{ \frac{4}{3} \rho^{(2)}(\underline{r}) [\rho^{(0)}(\underline{r})]^{1/3} + \frac{2 [\rho^{(1)}(\underline{r})]^2}{[\rho^{(0)}(\underline{r})]^{2/3}} \right\} \end{aligned} \quad (4.17)$$

From Eqs. (4.12c) and (3.17) we obtain the result that

$$\begin{aligned} \sum_{\mu} \theta_{\mu} \langle \mu | H^{(2)} | \mu \rangle = \sum_{\mu} \theta_{\mu} \langle \mu | V^{(2)} | \mu \rangle \\ + e^2 \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho^{(0)}(\underline{r}_1) \rho^{(2)}(\underline{r}_2)}{r_{12}} \\ - \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \left\{ \rho^{(2)}(\underline{r}) [\rho^{(0)}(\underline{r})]^{1/3} - \right. \\ \left. - \frac{1}{3} \frac{[\rho^{(1)}(\underline{r})]^2}{[\rho^{(0)}(\underline{r})]^{2/3}} \right\}. \end{aligned} \quad (4.18)$$

At the same time we can write

$$\sum_{\mu} \theta_{\mu} \sum_{\nu}^1 \frac{|\langle \mu | H^{(1)} | \nu \rangle|^2}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} = \frac{1}{2} \sum_{\mu \nu}^1 \frac{\theta_{\mu} - \theta_{\nu}}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \langle \mu | H^{(1)} | \nu \rangle \langle \nu | H^{(1)} | \mu \rangle \quad (4.19)$$

But from Eq. (4.12b) we see that

$$\begin{aligned} \langle \nu | H^{(1)} | \mu \rangle = & \langle \nu | V^{(1)} | \mu \rangle + \\ & + e^2 \int d^3 \underline{r}_2 \rho^{(1)}(\underline{r}_2) \int d^3 \underline{r}_1 \psi_{\nu}^{(0)*}(\underline{r}_1) \frac{1}{r_{12}} \psi_{\mu}^{(0)}(\underline{r}_1) - \\ & - \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \frac{\rho^{(1)}(\underline{r})}{[\rho^{(0)}(\underline{r})]^{2/3}} \psi_{\nu}^{(0)*}(\underline{r}) \psi_{\mu}^{(0)}(\underline{r}). \quad (4.20) \end{aligned}$$

If we substitute Eq. (4.20) into Eq. (4.19), and make use of Eq. (4.14) we obtain

$$\begin{aligned} \sum_{\mu} \theta_{\mu} \sum_{\nu}^1 \frac{|\langle \mu | H^{(1)} | \nu \rangle|^2}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} = & \frac{1}{2} \sum_{\mu \nu}^1 \frac{\theta_{\mu} - \theta_{\nu}}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \langle \mu | H^{(1)} | \nu \rangle \langle \nu | V^{(1)} | \mu \rangle + \\ & + \frac{e^2}{2} \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \frac{\rho^{(1)}(\underline{r}_1) \rho^{(1)}(\underline{r}_2)}{r_{12}} \\ & - \frac{\lambda}{6} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \frac{[\rho^{(1)}(\underline{r})]^2}{[\rho^{(0)}(\underline{r})]^{2/3}} \quad (4.21) \end{aligned}$$

Combining Eqs. (4.17), (4.18), and (4.21), we obtain finally the simple result that

$$\epsilon_o^{(2)} = \sum_{\mu} \theta_{\mu} \langle \mu | V^{(2)} | \mu \rangle + \frac{1}{2} \sum_{\mu \nu} \frac{\theta_{\mu} - \theta_{\nu}}{E_{\mu}^{(0)} - E_{\nu}^{(0)}} \langle \mu | H^{(1)} | \nu \rangle \langle \nu | V^{(1)} | \mu \rangle \quad (4.22)$$

In all that follows we will consider only the second order energy shift $\epsilon_o^{(2)}$. The reason for this is that if we substitute Eq. (4.3b) into the expression (4.16) for the first order energy shift $\epsilon_o^{(1)}$ and rewrite the result as

$$\epsilon_o^{(1)} = \sum_{\ell k \alpha} \Phi_{\alpha}^{(E)}(\ell k) u_{\alpha}(\ell k) \quad (4.23a)$$

where

$$\Phi_{\alpha}^{(E)}(\ell k) = - \int d^3 \underline{r} \rho^{(o)}(\underline{r}) \left\{ \frac{\partial}{\partial x_{\alpha}} U_{k \sim}(\underline{r} - \underline{x}(\ell k)) \right\}, \quad (4.23b)$$

the integral in Eq. (4.23b) vanishes if the point group of the lattice site (ℓk) is one of the following: C_1 , C_{2h} , D_2 , D_{2h} , S_4 , C_{4h} , S_{4v} , D_4 , D_{4h} , S_6 , D_3 , D_{3d} , C_{3h} , C_{6h} , D_{3h} , D_6 , D_{6h} , T , T_h , T_d , O , and O_h . This conclusion has its origin in the observation that the ion core potential $U_{k \sim}(\underline{r})$ must be invariant under the operations of the point group of the space group of the crystal if the zero-order potential $V^{(o)}(\underline{r})$ is to be invariant under the operations of the space group of the crystal. Inasmuch as we will be interested primarily in applying the results of this paper to crystals of the diamond structure, for which the site symmetry of any atom is that of the group T_d , the coefficient $\Phi_{\alpha}^{(E)}(\ell k)$ is identically

zero. It is convenient that this argument makes no use of any equilibrium condition. Of course, in the harmonic approximation the total first order atomic force constant $\Phi_{\alpha}(\ell k)$ must vanish if the crystal potential energy is expanded in powers of the nuclear displacements from the configuration of minimum potential energy. However, we have not attempted to determine the equilibrium configuration by minimizing the total potential energy of the crystal as calculated in the Hartree-Fock approximation, but instead have assumed the experimentally determined configuration, which may differ somewhat from that predicted by our necessarily approximate model. Consequently, for an arbitrary crystal, numerical evaluation of $\Phi_{\alpha}^{(E)}(\ell k)$ on the basis of Eq. (4.23b) could yield a non-zero answer. It is reassuring, therefore, that this cannot be the case for crystals of the diamond structure purely on the grounds of symmetry.

5. THE INTEGRAL EQUATION FOR $\langle \mu | H^{(1)} | \nu \rangle$

All of the functions entering into the expression for $\epsilon_o^{(2)}$ given by Eq. (4.22) are assumed to be known except for the operator $H^{(1)}$.

From Eq. (4.12b) we see that the first order valence charge density $\rho^{(1)}(\underline{r})$ appears in the definition of the operator $H^{(1)}$. At the same time we see from Eq. (4.14) that $H^{(1)}$ enters the expression for $\rho^{(1)}(\underline{r})$. This means that the matrix element $\langle \mu | H^{(1)} | \nu \rangle$ has to be determined self consistently.

If we substitute into Eq. (4.20) the expression (4.14) for $\rho^{(1)}(\underline{r})$, we can rewrite the result in the form of an integral equation for $\langle \mu | H^{(1)} | \nu \rangle$

$$\begin{aligned} \langle \mu | H^{(1)} | \nu \rangle = & \langle \mu | V^{(1)} | \nu \rangle + \\ & + \sum_{\sigma t}^1 \left[A_{\mu \nu \sigma t} - B_{\mu \nu \sigma t} \right] \frac{\theta_{\sigma} - \theta_t}{E_{\sigma}^{(0)} - E_t^{(0)}} \langle \sigma | H^{(1)} | t \rangle \end{aligned} \quad (5.1)$$

where

$$A_{\mu \nu \sigma t} = e^2 \int d^3 \underline{r}_1 \int d^3 \underline{r}_2 \psi_{\mu}^{(0)*}(\underline{r}_1) \psi_{\nu}^{(0)}(\underline{r}_1) \frac{1}{r_{12}} \psi_{\sigma}^{(0)}(\underline{r}_2) \psi_t^{(0)*}(\underline{r}_2) \quad (5.2a)$$

$$B_{\mu \nu \sigma t} = \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{1/3} \int d^3 \underline{r} \psi_{\mu}^{(0)*}(\underline{r}) \psi_{\nu}^{(0)}(\underline{r}) \left[\rho^{(0)}(\underline{r}) \right]^{-2/3} \times \psi_{\sigma}^{(0)}(\underline{r}) \psi_t^{(0)*}(\underline{r}) \quad (5.2b)$$

6. THE ELECTRONIC CONTRIBUTION TO THE DYNAMICAL MATRIX

The results of the preceding two sections take simpler and computationally more tractable forms if we exploit the periodicity of the perfect, unperturbed crystal described by the operator $H^{(0)}$. The principal consequence of this periodicity is that the eigenstates of $H^{(0)}$ are Bloch functions, which we denote by $\psi_{\underline{n}\underline{k}}(\underline{r})$, or by $|\underline{n}\underline{k}\rangle$ in expressions for matrix elements, where $\underline{k}$ is a wave vector which is confined to the first Brillouin zone of the crystal (reduced zone scheme) and n is a band index. It will be useful to keep in mind that $\psi_{\underline{n}\underline{k}}(\underline{r})$ can always be written in the form

$$\psi_{\underline{n}\underline{k}}(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} u_{\underline{n}\underline{k}}(\underline{r}), \quad (6.1)$$

where $u_{\underline{n}\underline{k}}(\underline{r})$ has the periodicity of the direct crystal, so that

$$\psi_{\underline{n}\underline{k}}(\underline{r} + \underline{x}(\underline{l})) = e^{i\underline{k} \cdot \underline{x}(\underline{l})} \psi_{\underline{n}\underline{k}}(\underline{r}). \quad (6.2)$$

The eigen-energy corresponding to the eigenstate $|\underline{n}\underline{k}\rangle$ will be denoted by $E_{\underline{n}\underline{k}}$.

We now rewrite the expression for $\mathcal{E}_0^{(2)}$ in terms of the Bloch functions and obtain explicit expressions for the atomic force constants of the crystal.

We denote the first term on the right hand side of Eq. (4.22) by $\mathcal{E}_0^{(21)}$:

$$\mathcal{E}_0^{(21)} = \sum_{\underline{n}\underline{k}} \theta(\underline{n}\underline{k}) \langle \underline{n}\underline{k} | V^{(2)} | \underline{n}\underline{k} \rangle. \quad (6.3)$$

If we express the bare ion potential $U_{\underline{k}}(\underline{r})$ as

$$U_{\underline{k}}(\underline{r}) = \frac{1}{(2\pi)^3} \int d^3 \underline{k} e^{-i \underline{k} \cdot \underline{r}} \hat{U}_{\underline{k}}(\underline{k}) \quad (6.4a)$$

$$\hat{U}_{\underline{k}}(\underline{k}) = \int d^3 \underline{r} e^{i \underline{k} \cdot \underline{r}} U_{\underline{k}}(\underline{r}), \quad (6.4b)$$

Then according to Eq. (4.3c) we have that

$$V^{(2)}(\underline{r}) = -\frac{1}{2} \sum_{\ell k \alpha \beta} u_{\alpha}(\ell k) u_{\beta}(\ell k) \frac{1}{(2\pi)^3} \int d^3 \underline{k} k_{\alpha} k_{\beta} e^{-i \underline{k} \cdot (\underline{r} - \underline{x}(\ell k))} \times \hat{U}_{\underline{k}}(\underline{k}). \quad (6.5)$$

Combining Eqs. (6.3) and (6.5) we can write $\mathcal{E}_o^{(21)}$ as

$$\mathcal{E}_o^{(21)} = -\frac{1}{2} \sum_{\ell k \alpha \beta} B_{\alpha \beta}(\ell k; \ell k) u_{\alpha}(\ell k) u_{\beta}(\ell k) \quad (6.6)$$

where

$$B_{\alpha \beta}(\ell k; \ell k) = \sum_{\underline{n} \underline{k}} \theta(\underline{n} \underline{k}) \frac{1}{(2\pi)^3} \int d^3 \underline{k}' k'_{\alpha} k'_{\beta} e^{i \underline{k}' \cdot \underline{x}(\ell k)} \times \hat{U}_{\underline{k}}(\underline{k}') \langle \underline{n} \underline{k} | e^{-i \underline{k}' \cdot \underline{r}} | \underline{n} \underline{k} \rangle. \quad (6.7)$$

The matrix element appearing in Eq. (6.7) can be rewritten in the following way:

$$\begin{aligned} \langle \underline{n} \underline{k} | e^{-i \underline{k}' \cdot \underline{r}} | \underline{n} \underline{k} \rangle &= \int d^3 \underline{r} \psi_{\underline{n} \underline{k}}^*(\underline{r}) e^{-i \underline{k}' \cdot \underline{r}} \psi_{\underline{n} \underline{k}}(\underline{r}) \\ &= \sum_{\ell} \int_{\Omega_{\ell}} d^3 \underline{r} \psi_{\underline{n} \underline{k}}^*(\underline{r}) e^{-i \underline{k}' \cdot \underline{r}} \psi_{\underline{n} \underline{k}}(\underline{r}) \end{aligned} \quad (6.8)$$

where the notation $\int_{\Omega_\ell}$ means that the integration is carried out over the volume of the ℓ^{th} primitive unit cell of the crystal. The change of variable $\underline{r} = \underline{x}(\ell) + \underline{\rho}$ together with Eq. (6.2) yields the result that

$$\langle n_{\underline{k}} | e^{-i \underline{k}' \cdot \underline{r}} | n_{\underline{k}} \rangle = \sum_{\ell} e^{-i \underline{k}' \cdot \underline{x}(\ell)} \int_{\Omega_0} d^3 \underline{\rho} \psi_{n_{\underline{k}}}^*(\underline{\rho}) e^{-i \underline{k}' \cdot \underline{\rho}} \quad (6.9)$$

We finally make use of the fact that

$$\sum_{\ell} e^{-i \underline{k} \cdot \underline{x}(\ell)} = \frac{(2\pi)^3}{\Omega_0} \sum_{\underline{G}} \delta(\underline{k} - \underline{G}) , \quad (6.10)$$

where $\underline{G}$ is 2π times a translation vector of the reciprocal lattice of the crystal and Ω_0 is the volume of a primitive unit cell of the direct lattice, to obtain

$$\langle n_{\underline{k}} | e^{-i \underline{k}' \cdot \underline{r}} | n_{\underline{k}} \rangle = (2\pi)^3 \sum_{\underline{G}} \delta(\underline{k}' - \underline{G}) \frac{1}{\Omega_0} \int_{\Omega_0} d^3 \underline{\rho} \psi_{n_{\underline{k}}}^*(\underline{\rho}) \psi_{n_{\underline{k}}}(\underline{\rho}) \times e^{-i \underline{G} \cdot \underline{\rho}} \quad (6.11)$$

Substituting Eq. (6.11) into Eq. (6.7), we obtain for $B_{\alpha\beta}(\ell k; \ell k)$

$$B_{\alpha\beta}(\ell k; \ell k) = \sum_{\underline{G}} G_{\alpha} G_{\beta} e^{i \underline{G} \cdot \underline{x}(\ell)} \hat{U}_{\underline{k}}(\underline{G}) \frac{1}{\Omega_0} \int_{\Omega_0} d^3 \underline{r} e^{-i \underline{G} \cdot \underline{r}} \rho_{\alpha\beta}^{(0)}(\underline{r}) , \quad (6.12)$$

where we have used Eq. (4.6a). The integral in Eq. (6.12) is recognized as the $\underline{G}^{\text{th}}$ Fourier coefficient of the unperturbed (i.e., static) valence electron number density in the crystal,

$$\rho^{(o)}(\underline{r}) = \sum_{\underline{G}} \hat{\rho}(\underline{G}) e^{i \underline{G} \cdot \underline{r}} \quad (6.13a)$$

$$\hat{\rho}(\underline{G}) = \frac{1}{\Omega_o} \int_{\Omega_o} d^3 \underline{r} e^{-i \underline{G} \cdot \underline{r}} \rho^{(o)}(\underline{r}) \quad (6.13b)$$

Thus, we obtain finally

$$\begin{aligned} B_{\alpha\beta}(\underline{l}k; \underline{l}k) &= \sum_{\underline{G}(\neq 0)} G_{\alpha} G_{\beta} e^{i \underline{G} \cdot \underline{x}^{(k)}} \hat{U}_k(\underline{G}) \hat{\rho}(\underline{G}) , \\ &= B_{\alpha\beta}^* (\underline{l}k; \underline{l}k) , \end{aligned} \quad (6.14)$$

where the restriction $\underline{G} \neq 0$ is due to our setting $\hat{U}_k(0) = 0$.

Turning now to the second term on the right hand side of Eq. (4.22), we rewrite it as

$$\begin{aligned} \mathcal{E}_o^{(22)} &= \frac{1}{2} \sum_{\underline{n}k} \sum_{\underline{n}'k'} \frac{\theta(\underline{n}k) - \theta(\underline{n}'k')}{E_{\underline{n}k} - E_{\underline{n}'k'}} < \underline{n}k | H^{(1)} | \underline{n}'k' > \times \\ &\times < \underline{n}'k' | V^{(1)} | \underline{n}k > . \end{aligned} \quad (6.15)$$

If we combine Eqs. (4.3b) and (6.4a) we find that

$$< \underline{n}k | V^{(1)} | \underline{n}'k' > = \frac{1}{(2\pi)^3} \int d^3 \underline{q} < \underline{n}k | e^{-i \underline{q} \cdot \underline{r}} | \underline{n}'k' > F_o(\underline{q}) \quad (6.16)$$

where

$$F_o(q) = u_\alpha(lk) i q_\alpha \hat{U}_k(q) e^{i q \cdot x(lk)} \quad (6.17)$$

Before we can substitute this expression into Eq. (6.15) we need an explicit expression for the matrix element $\langle nk | H^{(1)} | n'k' \rangle$. According to Eq. (5.1) this matrix element is the solution of the integral equation

$$\begin{aligned} \langle n \tilde{k} | H^{(1)} | n' \tilde{k}' \rangle &= \langle n \tilde{k} | V^{(1)} | n' \tilde{k}' \rangle + \\ &+ \sum_{n_1 \tilde{k}_1} \sum_{n_2 \tilde{k}_2} \left[A(n \tilde{k}, n' \tilde{k}'; n_1 \tilde{k}_1, n_2 \tilde{k}_2) - B(n \tilde{k}, n' \tilde{k}'; n_1 \tilde{k}_1, n_2 \tilde{k}_2) \right] \times \\ &\times \frac{\theta(n_1 \tilde{k}_1) - \theta(n_2 \tilde{k}_2)}{E_{n_1 \tilde{k}_1} - E_{n_2 \tilde{k}_2}} \langle n_1 \tilde{k}_1 | H^{(1)} | n_2 \tilde{k}_2 \rangle \end{aligned} \quad (6.18)$$

where

$$\begin{aligned} A(n \tilde{k}, n' \tilde{k}'; n_1 \tilde{k}_1, n_2 \tilde{k}_2) &= \int d^3 r_1 \int d^3 r_2 \psi_{n \tilde{k}}^*(r_1) \psi_{n' \tilde{k}'}(r_1) \frac{e^2}{r_{12}} \psi_{n_1 \tilde{k}_1}(r_2) \times \\ &\times \psi_{n_2 \tilde{k}_2}^*(r_2) \end{aligned} \quad (6.19a)$$

$$\begin{aligned} B(n \tilde{k}, n' \tilde{k}'; n_1 \tilde{k}_1, n_2 \tilde{k}_2) &= \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi} \right)^{\frac{1}{3}} \int d^3 r \psi_{n \tilde{k}}^*(r) \psi_{n' \tilde{k}'}(r) \left[\rho^{(o)}(r) \right]^{-\frac{2}{3}} \times \\ &\times \psi_{n_1 \tilde{k}_1}(r) \psi_{n_2 \tilde{k}_2}^*(r) \end{aligned} \quad (6.19b)$$

The solution of Eq. (6.18) with the inclusion of exchange is discussed in the Appendix. In the remainder of this section we work within the framework of the Hartree approximation and set

$$B(n \tilde{k}, n' \tilde{k}'; n_1 \tilde{k}_1, n_2 \tilde{k}_2) = 0.$$

If we introduce the Fourier transform of the Coulomb potential,

$$\frac{e^2}{r} = \frac{1}{(2\pi)^3} \int d^3 \underline{q} e^{-i \underline{q} \cdot \underline{r}} \hat{V}(\underline{q}) , \quad (6.20a)$$

$$\hat{V}(\underline{q}) = \frac{4\pi e^2}{q} , \quad (6.20b)$$

the kernel $A(\underline{n}k, \underline{n}'k'; \underline{n}_{1\sim 1}k_1, \underline{n}_{2\sim 2}k_2)$ can be rewritten in the simple form

$$\begin{aligned} A(\underline{n}k, \underline{n}'k'; \underline{n}_{1\sim 1}k_1, \underline{n}_{2\sim 2}k_2) &= \frac{1}{(2\pi)^3} \int d^3 \underline{q} \hat{V}(\underline{q}) \langle \underline{n}k | e^{-i \underline{q} \cdot \underline{r}} | \underline{n}'k' \rangle \times \\ &\times \langle \underline{n}_{2\sim 2}k_2 | e^{i \underline{q} \cdot \underline{r}} | \underline{n}_{1\sim 1}k_1 \rangle . \end{aligned} \quad (6.21)$$

The integral equation (6.17) therefore takes the form

$$\begin{aligned} \langle \underline{n}k | H^{(1)} | \underline{n}'k' \rangle &= \frac{1}{(2\pi)^3} \int d^3 \underline{q} \langle \underline{n}k | e^{-i \underline{q} \cdot \underline{r}} | \underline{n}'k' \rangle F_0(\underline{q}) + \\ &+ \frac{1}{(2\pi)^3} \int d^3 \underline{q} \langle \underline{n}k | e^{-i \underline{q} \cdot \underline{r}} | \underline{n}'k' \rangle \hat{V}(\underline{q}) \sum_{\underline{n}_{1\sim 1}k_1} \sum_{\underline{n}_{2\sim 2}k_2} \frac{\theta(\underline{n}_{1\sim 1}k_1) - \theta(\underline{n}_{2\sim 2}k_2)}{E_{\underline{n}_{1\sim 1}k_1} - E_{\underline{n}_{2\sim 2}k_2}} \times \\ &\times \langle \underline{n}_{2\sim 2}k_2 | e^{i \underline{q} \cdot \underline{r}} | \underline{n}_{1\sim 1}k_1 \rangle \langle \underline{n}_{1\sim 1}k_1 | H^{(1)} | \underline{n}_{2\sim 2}k_2 \rangle \end{aligned} \quad (6.22)$$

To solve this equation we make the obvious Ansatz

$$\langle \underline{n}k | H^{(1)} | \underline{n}'k' \rangle = \frac{1}{(2\pi)^3} \int d^3 \underline{q} \langle \underline{n}k | e^{-i \underline{q} \cdot \underline{r}} | \underline{n}'k' \rangle F(\underline{q}) \quad (6.23)$$

where the function $F(\underline{q})$ satisfies the integral equation

$$F(\underline{q}) = F_o(\underline{q}) + \hat{V}(\underline{q}) \int d^3 \underline{q}' X(\underline{q}, \underline{q}') F(\underline{q}') \quad (6.24)$$

with

$$X(\underline{q}, \underline{q}') = \frac{1}{(2\pi)^3} \sum_{\underline{n}_1 \underline{k}_1} \sum_{\underline{n}_2 \underline{k}_2} \frac{\theta(\underline{n}_1 \underline{k}_1) - \theta(\underline{n}_2 \underline{k}_2)}{E_{\underline{n}_1 \underline{k}_1} - E_{\underline{n}_2 \underline{k}_2}} < \underline{n}_2 \underline{k}_2 | e^{i \underline{q} \cdot \underline{r}} | \underline{n}_1 \underline{k}_1 > \times \\ \times < \underline{n}_1 \underline{k}_1 | e^{-i \underline{q}' \cdot \underline{r}} | \underline{n}_2 \underline{k}_2 > \quad (6.25)$$

The expression (6.15) for $\epsilon_o^{(22)}$ can be written compactly in terms of $X(\underline{q}, \underline{q}')$ as

$$\epsilon_o^{(22)} = \frac{1}{2} \frac{1}{(2\pi)^3} \int d^3 \underline{q} \int d^3 \underline{q}' X(\underline{q}, \underline{q}') F_o(-\underline{q}) F(\underline{q}') \quad (6.26)$$

Integration over all of $\underline{q}$ -space of a function $f(\underline{q})$ can be expressed alternatively as

$$\int d^3 \underline{q} f(\underline{q}) = \sum_{\underline{G}} \int_{BZ} d^3 \underline{q} f(\underline{q} + \underline{G}) , \quad (6.27)$$

where the integral on the right hand side of this equation is taken over only the first Brillouin zone of the crystal. With the aid of this relation Eq. (6.26) can be rewritten as

$$\epsilon_o^{(22)} = \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{\underline{G}, \underline{G}'} \int_{BZ} d^3 \underline{q} \int d^3 \underline{q}' X(\underline{q} + \underline{G}, \underline{q}' + \underline{G}') F_o(-\underline{q} - \underline{G}) \times \\ \times F(\underline{q}' + \underline{G}') . \quad (6.28)$$

In a manner similar to that in which Eq. (6.11) was established, it can be shown that

$$\begin{aligned}
\langle n_{\underline{k}} | e^{i(\underline{q} + \underline{G}) \cdot \underline{r}} | n'_{\underline{k}'} \rangle &= (2\pi)^3 \sum_{\underline{H}} \delta(\underline{k}' + \underline{q} - \underline{k} - \underline{H}) \times \\
&\times \frac{1}{\Omega_0} \int_{\Omega_0} d^3 \underline{r} \psi_{n_{\underline{k}}}^*(\underline{r}) e^{i(\underline{q} + \underline{G}) \cdot \underline{r}} \psi_{n'_{\underline{k}'}}(\underline{r}) \quad (6.29)
\end{aligned}$$

With the aid of this result it follows from Eq. (6.25) that $X(\underline{q} + \underline{G}, \underline{q}' + \underline{G}')$ has the form

$$X(\underline{q} + \underline{G}, \underline{q}' + \underline{G}') = \delta(\underline{q} - \underline{q}') X(\underline{q} + \underline{G}, \underline{q} + \underline{G}'), \quad (6.30)$$

when both $\underline{q}$ and $\underline{q}'$ are in the first Brillouin zone, where

$$\begin{aligned}
X_0(\underline{q} + \underline{G}, \underline{q} + \underline{G}') &= \frac{1}{\Omega} \sum_{n_1 \underline{k}_1} \sum_{n_2 \underline{k}_2} \frac{\theta(n_1 \underline{k}_1) - \theta(n_2 \underline{k}_2)}{E_{n_1 \underline{k}_1} - E_{n_2 \underline{k}_2}} \times \\
&\times \langle n_{2 \underline{k}_2} | e^{i(\underline{q} + \underline{G}) \cdot \underline{r}} | n_{1 \underline{k}_1} \rangle \langle n_{1 \underline{k}_1} | e^{-i(\underline{q} + \underline{G}') \cdot \underline{r}} | n_{2 \underline{k}_2} \rangle \quad (6.31a)
\end{aligned}$$

$$= \frac{(2\pi)^3}{\Omega} X(\underline{q} + \underline{G}, \underline{q} + \underline{G}'). \quad (6.31b)$$

Consequently, the expression for $\mathcal{E}_0^{(22)}$ simplifies to

$$\mathcal{E}_0^{(22)} = \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{\underline{G}, \underline{G}'} \int_{BZ} d^3 \underline{q} X_0(\underline{q} + \underline{G}, \underline{q} + \underline{G}') F_0(-\underline{q} - \underline{G}) F(\underline{q} + \underline{G}'), \quad (6.32)$$

while the integral equation (6.24) for $F(\underline{q} + \underline{G})$ reduces to a matrix equation

$$F(\underline{q} + \underline{G}) = F_0(\underline{q} + \underline{G}) + \hat{V}(\underline{q} + \underline{G}) \sum_{\underline{G}'} X_0(\underline{q} + \underline{G}, \underline{q} + \underline{G}') F(\underline{q} + \underline{G}'). \quad (6.33)$$

From the explicit expression for $X_0(\underline{q} + \underline{G}, \underline{q} + \underline{G}')$, Eq. (6.30b), we see that it has the following general properties:

$$X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}') = X_o^*(\underline{q}+\underline{G}', \underline{q}+\underline{G}) = X_o^*(-\underline{q}-\underline{G}, -\underline{q}-\underline{G}') . \quad (6.34)$$

Moreover, if the crystal has a center of inversion, and this point is chosen as the origin of coordinates, the transformation properties of Bloch functions under space group operations applied to the crystal⁽¹⁾ can be used to show that $X(\underline{q}+\underline{G}, \underline{q}+\underline{G}')$ is real in this case.

If we introduce a matrix $\epsilon(\underline{q})$ whose elements are given by

$$\epsilon(\underline{q}+\underline{G}, \underline{q}+\underline{G}') = \delta_{\underline{G}, \underline{G}'} - \hat{V}(\underline{q}+\underline{G}) X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}'), \quad (6.35)$$

the solution of Eq. (6.32) can be written formally as

$$F(\underline{q}+\underline{G}) = \sum_{\underline{G}'} \epsilon^{-1}(\underline{q}+\underline{G}, \underline{q}+\underline{G}') F_o(\underline{q}+\underline{G}'). \quad (6.36)$$

The inverse matrix elements $\{\epsilon^{-1}(\underline{q}+\underline{G}, \underline{q}+\underline{G}')\}$ are the solutions of the equation

$$\epsilon^{-1}(\underline{q}+\underline{G}, \underline{q}+\underline{G}') = \delta_{\underline{G}, \underline{G}'} + \sum_{\underline{G}''} \hat{V}(\underline{q}+\underline{G}) X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}'') \epsilon^{-1}(\underline{q}+\underline{G}'', \underline{q}+\underline{G}'). \quad (6.37)$$

It will be convenient in what follows to write $\epsilon^{-1}(\underline{q}+\underline{G}, \underline{q}+\underline{G}')$ in the form

$$\epsilon^{-1}(\underline{q}+\underline{G}, \underline{q}+\underline{G}') = \delta_{\underline{G}, \underline{G}_1} + \hat{V}(\underline{q}+\underline{G}) S(\underline{q}+\underline{G}, \underline{q}+\underline{G}'), \quad (6.38)$$

where the matrix element $S(\underline{q}+\underline{G}, \underline{q}+\underline{G}')$ can be expanded formally as

$$\begin{aligned} S(\underline{q}+\underline{G}, \underline{q}+\underline{G}') &= X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}') + \sum_{\underline{G}_1} X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}_1) V(\underline{q}+\underline{G}_1) X_o(\underline{q}+\underline{G}_1, \underline{q}+\underline{G}') \\ &+ \sum_{\underline{G}_1 \underline{G}_2} X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}_1) V(\underline{q}+\underline{G}_1) X_o(\underline{q}+\underline{G}_1, \underline{q}+\underline{G}_2) V(\underline{q}+\underline{G}_2) X_o(\underline{q}+\underline{G}_2, \underline{q}+\underline{G}') \\ &+ \dots \end{aligned} \quad (6.39)$$

It follows from Eq. (6.39) and the reality of $\hat{V}(\underline{q})$ that $S(\underline{q}+\underline{G}, \underline{q}+\underline{G}')$ has the properties expressed by Eq. (6.34), and is real when $X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}')$ is real.

Combining Eqs. (6.17), (6.31), and (6.36), we can write the ground state energy contribution $\mathcal{E}_o^{(22)}$ as

$$\mathcal{E}_o^{(22)} = \frac{1}{2} \sum_{\ell k \alpha} \sum_{\ell' k' \beta} A_{\alpha \beta}(\ell k; \ell' k') u_{\alpha}(\ell k) u_{\beta}(\ell' k') , \quad (6.40)$$

where

$$\begin{aligned} A_{\alpha \beta}(\ell k; \ell' k') &= \frac{1}{(2\pi)^3} \sum_{\underline{G} \underline{G}' \underline{G}''} \int_{\text{BZ}} d^3 \underline{q} X_o(\underline{q}+\underline{G}, \underline{q}+\underline{G}') \epsilon^{-1}(\underline{q}+\underline{G}', \underline{q}+\underline{G}'') \times \\ &\times (\underline{q}+\underline{G})_{\alpha} (\underline{q}+\underline{G}'')_{\beta} \hat{U}_{\underline{k}}(-\underline{q}-\underline{G}) e^{-i(\underline{q}+\underline{G}) \cdot \underline{x}(\underline{k})} \times \\ &\times \hat{U}_{\underline{k}'}(\underline{q}+\underline{G}'') e^{i(\underline{q}+\underline{G}'') \cdot \underline{x}(\underline{k}')} e^{-i \underline{q} \cdot (\underline{x}(\underline{\ell}) - \underline{x}(\underline{\ell}'))} \end{aligned} \quad (6.41a)$$

$$\begin{aligned} &= \frac{1}{(2\pi)^3} \sum_{\underline{G} \underline{G}'} \int_{\text{BZ}} d^3 \underline{q} S(\underline{q}+\underline{G}, \underline{q}+\underline{G}') (\underline{q}+\underline{G})_{\alpha} (\underline{q}+\underline{G}')_{\beta} \times \\ &\times \hat{U}_{\underline{k}}(-\underline{q}-\underline{G}) e^{-i(\underline{q}+\underline{G}) \cdot \underline{x}(\underline{k})} \hat{U}_{\underline{k}'}(\underline{q}+\underline{G}') e^{i(\underline{q}+\underline{G}') \cdot \underline{x}(\underline{k}')} \times \\ &\times e^{-i \underline{q} \cdot (\underline{x}(\underline{\ell}) - \underline{x}(\underline{\ell}'))} \end{aligned} \quad (6.41b)$$

$$= A_{\beta \alpha}(\ell' k'; \ell k) A_{\alpha \beta}^*(\ell k; \ell' k') . \quad (6.41c)$$

Combining Eqs. (6.6) and (6.40), we obtain for the contribution to the ground state energy of the electronic system which is quadratic in the nuclear displacements

$$\mathcal{E}_o^{(2)} = \frac{1}{2} \sum_{\ell k \alpha} \sum_{\ell' k' \beta} \alpha_{\beta}^{(\ell k; \ell' k')} u_{\alpha}(\ell k) u_{\beta}(\ell' k') \quad (6.42)$$

where

$$\alpha_{\beta}^{(\ell k; \ell' k')} = A_{\alpha\beta}^{(\ell k; \ell' k')} - \delta_{\ell\ell'} \delta_{kk'} B_{\alpha\beta}^{(\ell k; \ell k)} \quad (6.43)$$

The electronic contribution to the atomic force constant $\alpha_{\beta}^{(\ell k; \ell' k')}$,

(E) $\alpha_{\beta}^{(\ell k; \ell' k')}$ is seen to be real, and symmetric in the interchange of $(\ell k \alpha)$ and $(\ell' k' \beta)$.

The elements of the dynamical matrix of the crystal are defined by

$$D_{\alpha\beta}^{(k; kk')} = \frac{1}{(M_k M_{k'})^{1/2}} \sum_{\ell'} \alpha_{\beta}^{(\ell k; \ell' k')} e^{-i\mathbf{k} \cdot (\mathbf{x}(\ell) - \mathbf{x}(\ell'))} \quad (6.44)$$

The electronic contribution to the elements of the dynamical matrix are therefore given by

$$\begin{aligned} D_{\alpha\beta}^{(E)}(k; kk') &= \frac{1}{(M_k M_{k'})^{1/2}} \frac{1}{\Omega_0} \sum_{\mathbf{G}, \mathbf{G}'} S(-\mathbf{k}+\mathbf{G}, -\mathbf{k}+\mathbf{G}') (\mathbf{k}-\mathbf{G})_{\alpha} (\mathbf{k}-\mathbf{G}')_{\beta} \times \\ &\times \hat{U}_{\mathbf{k}}(\mathbf{k}-\mathbf{G}) e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{x}(\mathbf{k})} \hat{U}_{\mathbf{k}'}(-\mathbf{k}+\mathbf{G}') e^{-i(\mathbf{k}-\mathbf{G}') \cdot \mathbf{x}(\mathbf{k}')} - \\ &- \frac{\delta_{kk'}}{M_k} \sum_{\mathbf{G}(\neq 0)} G_{\alpha} G_{\beta} e^{i\mathbf{G} \cdot \mathbf{x}(\mathbf{k})} \hat{U}_{\mathbf{k}}(\mathbf{G}) \rho(\mathbf{G}) \quad (6.45) \end{aligned}$$

In the next section this expression will be simplified somewhat.

7. INFINITESIMAL TRANSLATION INVARIANCE AND THE SMALL q LIMIT OF THE ELECTRONIC CONTRIBUTION TO THE DYNAMICAL MATRIX

It is a general property of atomic force constants that⁽¹⁾

$$\sum_{l'k'} \Phi_{\alpha\beta}(lk; l'k') = 0. \quad (7.1)$$

This condition follows from the physical requirement that the net force on an atom does not change when the crystal is subjected to an infinitesimal rigid body displacement. The Coulomb contribution to the atomic force constants automatically satisfies Eq. (7.1) because it is derived from a two body potential. It follows, therefore, that the electronic contribution to the atomic force constants must satisfy the condition

$$\sum_{l'k'}^{(E)} \Phi_{\alpha\beta}(lk; l'k') = 0. \quad (7.2)$$

When Eq. (6.43) is substituted into Eq. (7.2), we obtain the following relation between $A_{\alpha\beta}(lk; l'k')$ and $B_{\alpha\beta}(lk; lk)$:

$$B_{\alpha\beta}(lk; lk) = \sum_{l'k'} A_{\alpha\beta}(lk; l'k') \quad (7.3)$$

We now show that our expressions for $B_{\alpha\beta}(lk; lk)$ and $A_{\alpha\beta}(lk; l'k')$, Eqs. (6.14) and (6.41), respectively, satisfy Eq. (7.3).

From Eqs. (6.41b) and (6.10) we find that

$$\sum_{\ell'k'} A_{\alpha\beta}(\ell k; \ell'k') = \sum_{\underline{G} \underline{G}'} S(\underline{G}, \underline{G}') G_{\alpha} G'_{\beta} \hat{U}_k(-\underline{G}) \times$$

$$\times e^{-i\underline{G} \cdot \underline{x}(k)} \frac{1}{\Omega_0} \sum_{k'} \hat{U}_{k'}(\underline{G}') e^{i\underline{G}' \cdot \underline{x}(k')} \quad (7.4)$$

Inasmuch as we have defined $\hat{U}_k(\underline{G} = 0)$ to be zero, we can exclude the terms corresponding to $\underline{G} = 0$ and $\underline{G}' = 0$ from the sums on the right hand side of Eq. (7.4).

The periodic bare electron-ion potential of the static lattice $V^{(o)}(\underline{r})$, which is defined by Eq. (4.3a), can be expanded in a Fourier series as

$$V^{(o)}(\underline{r}) = \sum_{\underline{G}} \hat{V}^{(o)}(\underline{G}) e^{i\underline{G} \cdot \underline{r}} \quad (7.5a)$$

with

$$V^{(o)}(\underline{G}) = \frac{1}{\Omega_0} \sum_k \hat{U}_k(-\underline{G}) e^{-i\underline{G} \cdot \underline{x}(k)} \quad (7.5b)$$

Similarly, the Hartree potential seen by the valence electrons in the static lattice,

$$V_H^{(o)}(\underline{r}) = e^2 \int d^3 \underline{r}' \frac{\rho^{(o)}(\underline{r}')}{|\underline{r} - \underline{r}'|}, \quad (7.6)$$

can also be expanded in a Fourier series,

$$V_H^{(o)}(\underline{r}) = \sum_{\underline{G}} \hat{V}_H^{(o)}(\underline{G}) e^{i\underline{G} \cdot \underline{r}}, \quad (7.7a)$$

where

$$\hat{V}_H^{(o)}(\underline{G}) = \hat{\rho}(\underline{G}) \hat{V}(-\underline{G}) . \quad (7.7b)$$

The total self-consistent potential seen by the valence electrons,

$$V_s(\underline{r}) = V^{(o)}(\underline{r}) + V_H^{(o)}(\underline{r}) , \quad (7.8)$$

therefore possesses the Fourier expansion

$$V_s(\underline{r}) = \sum_{\underline{G}} \hat{V}_s(\underline{G}) e^{i \underline{G} \cdot \underline{r}} \quad (7.9a)$$

with

$$\hat{V}_s(\underline{G}) = \frac{1}{\Omega_0} \sum_k \hat{U}_k(-\underline{G}) e^{-i \underline{G} \cdot \underline{x}(k)} + \hat{\rho}(\underline{G}) \hat{V}(-\underline{G}) . \quad (7.9b)$$

We now use the preceding results to establish the relation

$$\sum_{\underline{G}'} [\epsilon^{-1}(\underline{G}, \underline{G}') - \delta_{\underline{G}\underline{G}'}] G'_\alpha \hat{V}^{(o)}(-\underline{G}') = G_\alpha \hat{V}_H^{(o)}(-\underline{G}) , \quad (7.10)$$

with the aid of which we will establish Eq. (7.3).

We begin by writing the equation for $\psi_{n\tilde{k}}(\underline{r})$ in the Hartree approximation as

$$\left[\frac{p^2}{2m} + V_s(\underline{r}) \right] |n\tilde{k}\rangle = E_{n\tilde{k}} |n\tilde{k}\rangle . \quad (7.11)$$

We now take the partial derivative of both sides of this equation with respect to x_α to obtain

$$\frac{p^2}{2m} \frac{\partial}{\partial x_\alpha} |nk\rangle + V_s(\underline{r}) \frac{\partial}{\partial x_\alpha} |nk\rangle + \frac{\partial V_s(\underline{r})}{\partial x_\alpha} |nk\rangle = E_{nk} \frac{\partial}{\partial x_\alpha} |nk\rangle \quad (7.12)$$

If we multiply this equation from the left by $\psi_{n'k'}^*(\underline{r})$ and integrate over $\underline{r}$, we obtain

$$\langle n'k' | H \frac{\partial}{\partial x_\alpha} |nk\rangle + \langle n'k' | \frac{\partial V_s}{\partial x_\alpha} |nk\rangle = E_{nk} \langle n'k' | \frac{\partial}{\partial x_\alpha} |nk\rangle$$

or

$$\langle n'k' | \frac{\partial V_s}{\partial x_\alpha} |nk\rangle = [E_{nk} - E_{n'k'}] \langle n'k' | \frac{\partial}{\partial x_\alpha} |nk\rangle. \quad (7.13)$$

With the use of Eq. (7.9a) we can rewrite Eq. (7.13) as

$$i \sum_{\underline{G}} \langle n'k' | e^{i\underline{G} \cdot \underline{r}} |nk\rangle G_\alpha \hat{V}_s(\underline{G}) = [E_{nk} - E_{n'k'}] \langle n'k' | \frac{\partial}{\partial x_\alpha} |nk\rangle \quad (7.14)$$

Because $\underline{k}$ and $\underline{k}'$ are restricted to lie in the first Brillouin zone, both sides of Eq. (7.14) vanish unless $\underline{k} = \underline{k}'$, but we will not use this fact for the time being.

From Eq. (6.31a) we find that

$$\begin{aligned} X_o(\underline{G}, \underline{G}') &= \frac{1}{\Omega} \sum_{\underline{n}\underline{k}} \sum_{\underline{n}'\underline{k}'} \frac{\theta(\underline{n}\underline{k}) - \theta(\underline{n}'\underline{k}')}{E_{\underline{n}\underline{k}} - E_{\underline{n}'\underline{k}'}} \langle \underline{n}'\underline{k}' | e^{i\underline{G} \cdot \underline{r}} | \underline{n}\underline{k} \rangle \times \\ &\times \langle \underline{n}\underline{k} | e^{-i\underline{G}' \cdot \underline{r}} | \underline{n}'\underline{k}' \rangle. \end{aligned} \quad (7.15)$$

It follows on combining Eqs. (7.14) and (7.15) that

$$\begin{aligned}
\sum_{\underline{G}'} X_o(\underline{G}, \underline{G}') G'_\alpha \hat{V}_s(-\underline{G}') &= \frac{i}{\Omega} \sum_{\underline{n} \underline{k}} \sum_{\underline{n}' \underline{k}'} [\theta(\underline{n} \underline{k}) - \theta(\underline{n}' \underline{k}')] \times \\
&\quad \times \langle \underline{n}' \underline{k}' | e^{i \underline{G} \cdot \underline{r}} | \underline{n} \underline{k} \rangle \langle \underline{n} \underline{k} | \frac{\partial}{\partial x_\alpha} | \underline{n}' \underline{k}' \rangle \\
&= - \frac{i}{\Omega} \sum_{\underline{n} \underline{k}} \sum_{\underline{n}' \underline{k}'} \theta(\underline{n} \underline{k}) \{ \langle \underline{n} \underline{k} | \frac{\partial}{\partial x_\alpha} | \underline{n}' \underline{k}' \rangle \langle \underline{n}' \underline{k}' | e^{i \underline{G} \cdot \underline{r}} | \underline{n} \underline{k} \rangle - \\
&\quad - \langle \underline{n} \underline{k} | e^{i \underline{G} \cdot \underline{r}} | \underline{n}' \underline{k}' \rangle \langle \underline{n}' \underline{k}' | \frac{\partial}{\partial x_\alpha} | \underline{n} \underline{k} \rangle \} \\
&= - \frac{i}{\Omega} \sum_{\underline{n} \underline{k}} \theta(\underline{n} \underline{k}) \langle \underline{n} \underline{k} | [\frac{\partial}{\partial x_\alpha}, e^{i \underline{G} \cdot \underline{r}}] | \underline{n} \underline{k} \rangle \\
&= \frac{1}{\Omega} \sum_{\underline{n} \underline{k}} \theta(\underline{n} \underline{k}) \langle \underline{n} \underline{k} | e^{i \underline{G} \cdot \underline{r}} | \underline{n} \underline{k} \rangle G_\alpha \\
&= G_\alpha \hat{\rho}(-\underline{G}) .
\end{aligned} \tag{7.16}$$

If we set $\underline{q} = 0$ in Eq. (6.35), the resulting equation together with Eqs. (7.8) and (7.16) yields the relation

$$\sum_{\underline{G}'} \epsilon(\underline{G}, \underline{G}') G'_\alpha \hat{V}_s(-\underline{G}') = G_\alpha \hat{V}^{(0)}(-\underline{G}) . \tag{7.17}$$

We now multiply both sides of this equation by $\epsilon^{-1}(\underline{G}'', \underline{G})$ and sum over $\underline{G}$ to obtain

$$\sum_{\underline{G}} \epsilon^{-1}(\underline{G}'', \underline{G}) G_\alpha \hat{V}^{(0)}(-\underline{G}) = G''_\alpha \hat{V}_s(-\underline{G}'') . \tag{7.18}$$

In view of Eq. (7.8) we see that Eq. (7.10) follows directly from Eq. (7.18).

The proof of Eq. (7.3) now proceeds trivially. With the aid of Eqs. (6.38), (7.5b), and (7.7b), we rewrite Eq. (7.10) as

$$\widehat{V}(\underline{G}) \sum_{\underline{G}'} S(\underline{G}\underline{G}') G'_{\alpha} \frac{1}{\Omega_0} \sum_{\underline{k}'} \widehat{U}_{\underline{k}'}(\underline{G}') e^{i \underline{G}' \cdot \underline{x}(\underline{k}')} = G_{\alpha} \rho(-\underline{G}) \widehat{V}(\underline{G}). \quad (7.19)$$

When we substitute this result into the right hand side of Eq. (7.4) we obtain

$$\begin{aligned} \sum_{\ell' \underline{k}'} A_{\alpha\beta}(\ell \underline{k}; \ell' \underline{k}') &= \sum_{\underline{G}} G_{\alpha} \widehat{U}_{\underline{k}}(-\underline{G}) e^{-i \underline{G} \cdot \underline{x}(\underline{k})} G_{\beta} \widehat{\rho}(-\underline{G}) \\ &= B_{\alpha\beta}(\ell \underline{k}; \ell \underline{k}), \end{aligned} \quad (7.20)$$

according to Eq. (6.14). (E)

It follows, therefore, that we can write $\alpha\beta(\ell \underline{k}; \ell' \underline{k}')$ as

$$\alpha\beta(\ell \underline{k}; \ell' \underline{k}') = A_{\alpha\beta}(\ell \underline{k}; \ell' \underline{k}') - \delta_{\ell\ell'} \delta_{\underline{k}\underline{k}'} \sum_{\ell'' \underline{k}''} A_{\alpha\beta}(\ell \underline{k}; \ell'' \underline{k}''), \quad (7.21)$$

in which form the validity of Eq. (7.2) is manifest.

Combining Eqs. (6.45) and (7.19), we can write the electronic contribution to the dynamical matrix in the following form:

$$\begin{aligned} D_{\alpha\beta}^{(E)}(\underline{k}; \underline{k}\underline{k}') &= \frac{1}{(M_{\underline{k}} M_{\underline{k}'})^{1/2}} \frac{1}{\Omega_0} \sum_{\underline{G}, \underline{G}'} S(-\underline{k}+\underline{G}, -\underline{k}+\underline{G}') (\underline{k}-\underline{G})_{\alpha} (\underline{k}-\underline{G}')_{\beta} \times \\ &\times \widehat{U}_{\underline{k}}(\underline{k}-\underline{G}) e^{i(\underline{k}-\underline{G}) \cdot \underline{x}(\underline{k})} \widehat{U}_{\underline{k}'}(-\underline{k}+\underline{G}') e^{-i(\underline{k}-\underline{G}') \cdot \underline{x}(\underline{k}')} \\ &- \delta_{\underline{k}\underline{k}'} \sum_{\underline{k}''} \frac{1}{M_{\underline{k}}} \frac{1}{\Omega_0} \sum_{\underline{G}, \underline{G}'} S(\underline{G}, \underline{G}') G_{\alpha} G'_{\beta} \widehat{U}_{\underline{k}}(-\underline{G}) e^{-i \underline{G} \cdot \underline{x}(\underline{k})} \times \\ &\times \widehat{U}_{\underline{k}''}(\underline{G}') e^{i \underline{G}' \cdot \underline{x}(\underline{k}'')} \end{aligned}$$

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APPENDIX

The only approximation which renders the solution of the integral equation 6.18 analytically tractable with the inclusion of exchange seems to be to replace the valence charge density $\rho^{(o)}(\underline{r})$ in the integrand of Eq. 6.19b by a constant value ρ_o . With this approximation the expression for the coefficient $B(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1, \underline{n}_2\underline{k}_2)$ can be written as

$$B(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1, \underline{n}_2\underline{k}_2) = \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi\rho_o} \right)^{1/3} \times$$

$$\times \int d^3\underline{r}_1 \int d^3\underline{r}_2 \psi_{\underline{n}\underline{k}}^*(\underline{r}_1) \psi_{\underline{n}'\underline{k}'}(\underline{r}_1) \delta(\underline{r}_1 - \underline{r}_2) \times$$

$$\times \psi_{\underline{n}_1\underline{k}_1}(\underline{r}_2) \psi_{\underline{n}_2\underline{k}_2}^*(\underline{r}_2)$$
(A.1)

If we introduce the Fourier integral representation of the Dirac delta-function,

$$\delta(\underline{r}) = \frac{1}{(2\pi)^3} \int d^3\underline{q} e^{-i\underline{q} \cdot \underline{r}},$$
(A.2)

Eq. A.1 takes the simple form ,

$$B(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1; \underline{n}_2\underline{k}_2) = \frac{\lambda}{3} e^{2\left(\frac{3}{8\pi\rho_o}\right)^{1/3}} \times$$

(A.3)

$$\times \frac{1}{(2\pi)^3} \int d^3\underline{q} \langle \underline{n}\underline{k} | e^{-i\underline{q} \cdot \underline{r}} | \underline{n}'\underline{k}' \rangle \langle \underline{n}_2\underline{k}_2 | e^{i\underline{q} \cdot \underline{r}} | \underline{n}_1\underline{k}_1 \rangle .$$

Comparing this result with that for the kernel $A(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1, \underline{n}_2\underline{k}_2)$ we see that with the present approximation we can include the effects of exchange in the derivations given in the text by replacing $\hat{V}(\underline{q})$ by $\hat{V}(\underline{q}) [1 - f(\underline{q})]$ in Eqs. 6.38 and 6.39, where

$$f(\underline{q}) = 2\lambda \frac{q^2}{(8\pi)^{4/3} (3\rho_o^2)^{2/3}} \quad (\text{A.4})$$

As it stands, Eq. A.4 for $f(\underline{q})$ has the disagreeable feature that it exceeds unity for $q > (8\pi)^{2/3} (3\rho_o^2)^{1/3} / (2\lambda)^{1/2}$, forcing $V(\underline{q})(1-f(\underline{q}))$ to become negative. However, for large values of $\underline{q}$ we expect the exchange term to reduce the direct coulomb interaction by a factor of two, so that we regard Eq. A.4 as an approximation to a more accurate expression

$$f(\underline{q}) = \frac{1}{2} \frac{q^2}{(8\pi)^{4/3} (e\rho_o^2)^{2/3}} \frac{1}{4\lambda + q^2}$$

in the limit as $\underline{q} \rightarrow 0$.

$$A(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1, \underline{n}_2\underline{k}_2) - B(\underline{n}\underline{k}, \underline{n}'\underline{k}'; \underline{n}_1\underline{k}_1, \underline{n}_2\underline{k}_2)$$

$$= \frac{1}{(2\pi)^3} \int d^3 \underline{q} \hat{V}(\underline{q}) \langle \underline{n}\underline{k} | e^{-i\underline{q} \cdot \underline{r}} | \underline{n}'\underline{k}' \rangle \langle \underline{n}_2\underline{k}_2 | e^{i\underline{q} \cdot \underline{r}} | \underline{n}_1\underline{k}_1 \rangle$$

$$- \frac{1}{(2\pi)^3} \int d^3 \underline{q} \left[\frac{\lambda}{3} e^2 \left(\frac{3}{8\pi\rho_o^2} \right)^{1/3} \right] \langle \underline{n}\underline{k} | e^{-i\underline{q} \cdot \underline{r}} | \underline{n}'\underline{k}' \rangle \times$$

$$\times \langle \underline{n}_2\underline{k}_2 | e^{i\underline{q} \cdot \underline{r}} | \underline{n}_1\underline{k}_1 \rangle$$

$$= \frac{1}{(2\pi)^3} \int d^3 \underline{q} \left[\hat{V}(\underline{q}) - \frac{\lambda}{3} e^2 \left(\frac{3}{8\pi\rho_o^2} \right)^{1/3} \right] \times$$

$$\times \langle \underline{n}\underline{k} | e^{-i\underline{q} \cdot \underline{r}} | \underline{n}'\underline{k}' \rangle \langle \underline{n}_2\underline{k}_2 | e^{i\underline{q} \cdot \underline{r}} | \underline{n}_1\underline{k}_1 \rangle$$

$$= \frac{1}{(2\pi)^3} \int d^3 \underline{q} \hat{V}(\underline{q}) [1 - f(\underline{q})] \times$$

$$f(\underline{q}) = \frac{\lambda}{3} \left(\frac{3}{8\pi\rho_o^2} \right)^{1/3} \frac{q^2}{4\pi}$$

$$= \frac{2}{3} \lambda \left(\frac{3}{8\pi\rho_o^2} \right)^{1/3} \frac{q^2}{[(8\pi)^3]^{1/3}}$$

$$= \frac{2}{3} \lambda \left(\frac{3}{(8\pi)^4 \rho_o^2} \right)^{1/3} q^2$$

$$= \frac{2}{3} \lambda \frac{3^{1/3}}{(8\pi)^{4/3} \rho_o^{2/3}}$$

$$= 2\lambda \frac{q^2}{(8\pi)^{4/3} (3\rho_o^2)^{2/3}} \approx 2\lambda \frac{q^2}{(8\pi)^{4/3} (3\rho_o^2)^{2/3} + 4\lambda q^2}$$

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SPATIALLY DEPENDENT RESONANCE NEUTRON SPECTRA
IN A SLAB OF DEPLETED URANIUM

by

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APPENDIX B

SPATIALLY DEPENDENT RESONANCE NEUTRON SPECTRA
IN A SLAB OF DEPLETED URANIUM

H. M. Antunez and J. M. Neill

1. INTRODUCTION

In this paper, we describe position-dependent spectral measurements in the resolved resonance energy range across a thick slab of depleted uranium placed between two slabs of boron-loaded polyethylene. These measurements were undertaken to demonstrate that techniques developed at Gulf General Atomic^(1, 2) and elsewhere^(3, 4, 5) for measuring thermal neutron spectra in heterogeneous systems could be refined for use in media having strong resonances and large flux anisotropies. The results of the measurements were of interest because there were very little differential spectral data that could be used to confirm the adequacy of the calculational methods commonly used for reactor design in the resolved resonance energy region. It was of particular interest⁽⁶⁾ to compare the experimental data to the predictions of the discrete ordinates transport theory code 1DF⁽⁷⁾ and to intercompare that code's predictions to those of the resonance absorption code, GAROL⁽⁸⁾. The code GAROL has certain simplifying assumptions that it was desired to check. These are that the inelastic scattering by the absorber medium can be neglected and that the collision escape probabilities for each region in the cell can be computed on the basis of a flat source distribution. The latter would be tested with the use of a thick (3.14 cms) absorber slab of depleted uranium. It was also deemed worthwhile to explore the circumstances under which an infinite medium code such as GAROL could be applied to the solution of the space-integrated, energy-dependent neutron spectra in a finite geometry such as the one employed here.

The experiment has also motivated the studies of various quadrature sets in 1DF. This was of special interest here because the highly anisotropic fluxes observed in this experiment are not source induced,

but arise as a consequence of the different properties of the adjacent media. In addition, the analysis of the experimental data has led to studies of the sensitivity of the calculated fluxes to the spatial and energy representation in 1DF, and to the cross section averaging procedures. Finally, the strong flux gradients in the system were expected to amplify any perturbations in the spectra caused by the presence of the reentrant hole from which the flux was extracted. There has long been a dearth of reliable information on this perturbation, and this knowledge would support the heterogeneous spectral measurements presently being made⁽⁹⁾ at thermal energies.

2. EXPERIMENT

The time-integrated spectral measurements reported here were performed by standard time-of-flight means^(1, 2, 10) utilizing the Gulf General Atomic Electron Linear Accelerator to provide a pulsed source of neutrons. The experimental configuration, illustrated in Fig. 1, consisted of a 30.5 cm by 30.5 cm by 3.14 cm thick slab of depleted uranium (0.23% ^{235}U) which was placed between two slabs of polyethylene each 30.5 cm x 30.5 cm x 2.49 cm thick. A slab geometry was chosen in order to simplify the analysis of the problem. The polyethylene was loaded with boron to 5.3 wt %. Uranium-238 was chosen as the resonance absorber in this work because of its ready availability, convenient resonance width and level spacing, and because its cross sections were well known. The moderator (borated polyethylene) was chosen so as to combine a small slowing-down time and high absorption to insure a short mean emission time of the neutrons from the system and hence adequate energy resolution for these studies. In addition, the borated polyethylene made the leakage small relative to the absorption. This configuration did not represent a cell in a semi-infinite array, but there were insufficient uranium slabs available to approximate that array.

Figure 1. Geometry for resonance region spectral studies in depleted uranium.

The pulsed photo-neutron source was produced by impinging electrons from the LINAC onto a water-cooled fansteel (tungsten alloy) target. These neutrons were spread spatially by a 1.27-cm thick slab of iron before exciting the assembly. The fast neutrons were slowed down in the system and extracted from a 1.27-cm diameter reentrant hole located at 7.0 cm from the edge. A precollimator diameter of 1.05 cm was found to provide satisfactory counting rates. (A 0.95-cm diameter reentrant hole in conjunction with a 0.76-cm diameter precollimator was used initially and found to give unacceptably low count rates.) The position of the reentrant hole was chosen to be as close as possible to the source, to increase the observed flux intensities, but far enough so that the higher flux harmonics would have small magnitudes. The adequacy of the compromise of these two conditions is reflected in Fig. 2 by comparison at the measurement position of the axial flux plots using dysprosium-aluminum and cadmium-covered manganese and indium foils. The slopes of the curves are not greatly dissimilar at the measurement position of 7.0 cms, indicating that the flux harmonics are small in the energy response range of these foils. Flux plots with cadmium-covered indium foils were measured in the other two directions to permit the local buckling to be determined. In addition, the flux plot in the measurement direction, shown in Fig. 3, provided a spatial distribution for the slowing source in subsequent calculations.

The reentrant hole was in fact, a through hole into which plugs of the appropriate material and thickness were inserted to obtain the desired measurement positions. The neutrons were extracted from this hole and timed over an evacuated 16-meter flight path to their detection by a bank of 32 BF_3 counters. The data were recorded on a TMC-1024 channel analyzer using channel widths of 1 μsec . A background was measured by putting a B^{10} plug over the precollimator. The data were reduced to neutron spectra by means of the code HECTO⁽¹¹⁾ which corrects for the mean emission time, subtracts background, corrects for count rate losses, and incorporates the energy dependence of the detector sensitivity and the flight path transmission.

Figure 2. Foil activations along the source-assembly axis.

Figure 3. Cadmium-covered indium foil activations in the direction of the spectrum measurements

The spectral data taken were reduced incorporating the measured time-dependent background and a small constant background based on the residual counts at the bottom of the flux dip due to the 6.68 eV resonance in ^{238}U . It was of interest to identify the sources of this residual background and the following mechanisms were postulated:

1. Direct slowing down contribution to this energy from inelastic scattering in ^{238}U . This postulate was rejected since the computed energy transfer matrix indicated no such contribution.
2. Streaming effect in the reentrant hole. This postulate was examined by performing a subsidiary experiment in which the neutron spectrum at the center of the uranium slab was measured by time-of-flight with and without a depleted uranium sleeve (0.127-cm wall) placed inside the reentrant hole. This sleeve covered the polyethylene and prevented resonance energy neutrons from streaming into the uranium and scattering back down the flight path. No significant spectral differences were observed.
3. Delayed neutrons from fission in ^{235}U and ^{238}U . A dieaway experiment was performed to long times after the neutron burst, which permitted the ratio of prompt to delayed neutrons to be obtained. This ratio was much too small to provide a significant background at the 6.68 eV flux dip. The asymptotic dieaway of the system was found to be 10.1 μsecs , which is larger than the infinite medium dieaway of the borated polyethylene. In view of the very low multiplication of the system, the long dieaway must have been due to the long lifetime of thermal neutrons in the depleted uranium slab.

4. Pulsing overlap neutrons. These neutrons had been removed by a B_4C filter in the flight path.
5. Resolution broadening effects. The resolving time was estimated to be about 2 μ secs, derived from 1- μ sec resolution time for the BF_3 bank, 1 μ sec from the analyzer channel width and 0.3 μ sec from the standard deviation of the mean emission time. The latter was calculated with the methods given by Beckurts and Wirts⁽¹²⁾. The FWHM of the flux dip at the 6.68 eV resonance is approximately 20% in energy and this corresponds to a time spread of 45 μ secs. This value is so much larger than the resolving time (2 μ secs) of the measurement system that resolution broadening can be dismissed as a significant contributor to the residual counts at the resonance flux dip.
6. Alignment errors. Considerable care was taken in aligning the reentrant hole to the precollimator and flight path axis. Had there been much misalignment, the observed neutron spectra with and without the uranium sleeve would have displayed noticeable differences.
7. Room return neutrons. These neutrons would give rise to a signal with an apparent energy shift, and moreover would not be observed during the background run. The effects of these room return neutrons had been observed previously⁽¹³⁾ in σ_T measurements near the Bragg cutoff of various crystalline materials.

In view of the negligible shielding around the small experimental assembly, it is reasonable to ascribe the small residual background to room return neutrons. The value of the constant residual background

subtracted was adjusted at each position so that the measured and 1DF calculated neutron spectra were in agreement at the 6.68 eV resonance flux dip. Fortunately the agreement mentioned in Section 3 between the GAROL computed flux and the 1DF space averaged values gave some confidence in the magnitude of the computed flux dip. In addition, the value of the residual background was found consistently to be proportional to the monitor counts.

Experimental results for all measurement positions are compared with the calculations in Section 3. However, we show here, in Fig. 4, the time-of-flight neutron spectrum at the center of the depleted uranium slab throughout the whole energy range of the measurements. The points shown correspond to the 1- μ sec time channels of the multi-channel analyzer, except that they have been grouped below 135 eV to obtain an energy resolution of ~ 2 percent. The actual energy resolution, based on the 2- μ sec resolution time discussed previously is proportional to $(E)^{1/2}$, and amounts to 15% at 2 keV and 0.9% at 6.68 eV. The sensitivity of the near-zero flux at 6.68 eV to the value of the small constant background that is subtracted explains the very large statistical uncertainties observed at that level.

The measured spectra show a significant departure from a $1/E$ behavior between resonances because of the high leakage and strong absorption in the boron-loaded polyethylene. The flux is also strongly perturbed by the ^{238}U resonances below 100 eV. The flux depression due to the 8.8 eV resonance in ^{235}U can also be observed despite the low concentration (0.23 weight percent) of this isotope. (However, this depression is not displayed clearly in Fig. 4.)

3. CALCULATION

Limitations of computer memory precluded consideration of more than one dimension in calculating the space dependent neutron spectrum in our system. These computations were therefore performed with 1DF,

Figure 4. Time-of-flight neutron spectrum at Position 6 (the center of the uranium slab).

an S_n transport theory code. The planning of the transport calculations was based on a thorough study of the physics of the problem with the aid of preliminary experimental results. This led us to use a linearly anisotropic (P_1) scattering approximation, an isotropic volume distributed neutron source, and a compromise of the largest order of S_n and the best space and energy resolution possible. This compromise was achieved by first limiting the energy range of the calculation to a band around the strongest ^{238}U resonance, namely that at 6.68 eV. Symmetry about the uranium midplane was assumed. It was also considered desirable to restrict the spacing Δx according to the relationship below:

$$\Delta x < 3\lambda_{\min}/n$$

where n is the order of quadrature and $\lambda_{\min}$ the minimum total mean free path. The resulting compromise permitted 10 energy groups (down-scattering only), whose boundaries are given in Table I. This also allowed 608 space intervals (588 in the uranium and 20 in the polyethylene), in an S_6 calculation for a total of 64,400 words in memory. The space intervals were constant in the uranium but were variable in the polyethylene, decreasing close to the interface to allow for the increasing resonance flux gradient.

The code 1DF has the limitation that a "first interval vacuum, last reflective," boundary condition cannot be used. It was therefore desirable to use a quadrature which included the direction cosines, $\mu = +1, -1$, so as to be able to calculate in the half-system geometry all of the measured angular spectra. The Lobatto quadrature⁽¹⁴⁾ was selected because it meets that requirement. For the sake of checking it against frequently used quadratures, comparative 1DF runs were made with the set of direction cosines and corresponding weights⁽¹⁵⁾ built into 1DF, and with the Gauss-Legendre (P_n) set⁽¹⁶⁾, which takes as direction cosines the zeros of the Legendre polynomials. Two other comparative 1DF runs were performed using S_4

TABLE I
Broad Energy Group Boundaries for the IDF Calculations

<u>Group Number</u>	<u>Energy Interval (eV)</u>
1	11.0 - 9.0
2	9.0 - 7.6
3	7.6 - 7.2
4	7.2 - 6.99
5	6.99 - 6.76
6	6.76 - 6.6
7	6.6 - 6.1
8	6.1 - 5.8
9	5.8 - 4.5
10	4.5 - 3.3

rather than S_6 ; one of them with only 352 space intervals (336 in uranium and 16 in polyethylene), obtained from a less stringent largest interval condition:

$$\Delta x < 4\lambda_{\min}/n$$

All these 1DF runs were made with the same broad group cross sections and with the same energy dependence for neutron source. The parameters which varied from one to another and the largest total differences observed in the scalar and angular neutron fluxes calculated in the five runs are summarized in Table II. These maximum differences are not large and the typical differences have much smaller values. The point at which the calculated flux anisotropy was found to be largest is in the uranium, at 0.0053 cm from the interface and in energy group 6. Figure 5 displays the values of the angular flux as a function of the direction cosine at that energy and radius for the different runs having an interval mesh of 608 points. No interpolation curve has been drawn on the plot, since it is clear that the points lie approximately on a smooth curve. Therefore, an increase of the quadrature order to S_8 would not have been justified in view of the degree of agreement already achieved. The errors resulting from having used a quadrature of less than S_6 are already comparable to, or smaller than, those from other uncertainties in the problem, such as energy resolution, and knowledge of the source and cross sections.

The cross sections used for ^{238}U were Doppler broadened values obtained with the code FASDOP⁽¹⁷⁾ using the parameters of Ref. 18. The ^{235}U cross sections were from Ref. 19. The broad group averaging process was performed for the uranium slab with the two-region slowing down code GAROL. This procedure did not provide the slowing down kernel, and so this was separately computed in a P_0 approximation and averaged with the GAROL spectrum. An approximate P_1 slowing down kernel for the uranium was obtained by multiplying the corresponding P_0 term by a constant $\bar{\mu}$, the average cosine of the scattering angle.

ANGULAR FLUX
PER UNIT ENERGY
(RELATIVE UNITS)

Figure 5. The effect of different quadratures on the angular flux at the position and energy of maximum anisotropy

TABLE II

Largest Total Differences Observed in the Neutron Fluxes Calculated with the Code 1DF
Around the 6.63 eV Uranium Resonance for Different Spatial Meshes, S_n Approximations and Quadratures.

<u>Run</u>	<u>Mesh</u>	<u>S_n</u>	<u>Quadrature</u>	<u>Scalar Flux</u>		<u>Angular Flux, $\mu = -1$</u>		
				<u>Uranium</u>	<u>Polyethylene</u>	<u>Group 5</u>	<u>Group 6</u>	<u>Group 7</u>
4	352	4	1DF	10%	2%	< 1%	20%	< 1%
5	608	4	1DF	10%	1.5%	< 1%	4%	< 1%
6	608	6	1DF					
7	608	6	Lobatto	2.5%	< 1%	< 1%	2%	< 1%
8	608	6	P_n					

In the borated polyethylene region there are no rapidly changing cross sections in our range of interest. As a consequence, satisfactory broad group averages could be obtained in a single step with the infinite medium slowing down code GAR⁽²⁰⁾.

A correction to the total and absorption cross sections was made to account for transverse leakage, since 1DF is a one-dimensional code. The correction, $D(E) B^2$, was based on the epicadmium indium activation measurement and was found to be negative. This correction was found to be unimportant since it made a difference of at most 2% in the 1DF calculated flux, even though $D(E) B^2 / \Sigma_a$ was larger than 0.06 in the uranium for the broad energy groups 1 and 10. This justified the omission of transverse leakage considerations in the GAROL calculations, which will be discussed later.

Epicadmium indium activation measurements provided a spatial flux distribution which was used to calculate the volume distributed slowing down neutron source in both regions by means of the code DSZ⁽²¹⁾. This code also gave a $\phi(x, E)$ estimate as a byproduct, which allowed convergence of the 1DF runs to an over-all precision of 10^{-4} after only three outer iterations involving 91 inner (energy group) iterations. Improvement of this flux estimate by replacing it with an actual 1DF output reduced the number of inner iterations to 65. The 1DF runs were made with satisfactory results using a value of 10^{-4} for the over-all convergence precision. No oscillations or any other kind of qualitatively unexpected results were observed even for the 352 interval mesh.

The calculated fluxes were found to be sensitive to the weighting function used to average the cross sections in the broad groups only in the resonance wings. About 6% change in the width of the resonance angular flux dip was observed in a 1DF run for which the group cross sections had been averaged with a preliminary measured spectrum. The depth of the angular flux dip changed from 4.0×10^{-6} to 5.6×10^{-6} .

Figure 6 shows the spatial variation of the scalar flux calculated with the 1DF code. The small difference in the shape of the flux for groups 1 and 10 justifies the use of the epicadmium indium activation data to generate the spatial distribution of the neutron source for 1DF. The spatial dependence shown in Fig. 6 did not change appreciably for different 1DF runs in which cross sections based on different averaging fluxes had been used. The most striking feature of this figure is perhaps the drastic change (factor of 600) in the scalar flux in the first 0.03 cm of the uranium at the resonance energy, broad group 6.

The angular fluxes calculated by 1DF using GAROL cross sections are compared to the measured spectra in Figs. 7 and 8. Monitor normalization has been retained at each measurement position and the single normalization between theory and all the experimental data is obtained from the fit in the highest two energy groups at Position 3 only. The experimental values have been averaged over the broad energy group intervals for a more accurate comparison. The standard deviation of the measured fluxes is smaller than the radius of the dot except at the points where the error bars are drawn. The agreement between experiment and theory is shown to be reasonably good considering the broad group structure of the calculation. The figures display, in both theory and measurement, the systematic broadening of the resonance flux dip as the position moves further from the polyethylene source. There are, however, some significant discrepancies in energy groups 4 and 5, experiment being generally higher. The calculated fluxes below the resonance are consistently high by some 3%, which is large compared to the resonance absorption probability.

The space dependence of the resonance energy angular flux (group 6, $\mu = +1$) is shown in Fig. 9 and can be compared with the spatial behavior of groups 4, 5, and 7, which are on the resonance wings. Group 6 shows little of the spatial asymmetry away from the interface displayed

Figure 6. 1DF calculations of the spatially dependent scalar neutron flux across the uranium and borated polyethylene slabs

Figure 7. Comparison of calculated and measured neutron fluxes at Positions 1 through 5.

Figure 8. Comparison of calculated and measured neutron fluxes at Positions 6 through 9.

Figure 9. Comparison of the measured and calculated spatial distribution of the angular fluxes around 6.68 eV

by the other energy groups. This is because neutrons that downscatter in the uranium predominate in group 6. Nevertheless, at the uranium-polyethylene interface the resonance flux anisotropy is extreme as shown in Figs. 7 and 8 by the difference between the flux at positions 3 and 9.

There is a different spatial behavior of the flux in energy groups 4 and 5 (upper resonance wing) from that in group 7 (lower resonance wing), although the average cross sections for these wings are roughly similar. This has been interpreted as a consequence of only a few neutrons being downscattered in the uranium past the resonance into group 7 while groups 4 and 5 have a much greater downscattering source. Thus, the angular flux behavior in energy group 7 is dominated by neutrons leaking in from the polyethylene and the calculated flux therefore shows a strong exponential behavior over a large portion of the uranium slab. This calculated spatial distribution has an exponent which corresponds exactly to the average total cross section for energy group 7. The measured fluxes in group 7 show a somewhat different behavior. If interpreted in the same way, the measured exponents would lie between the point total cross sections corresponding to the energy group 7 boundaries. This indicates how the "actual" broad group cross section decreases as the neutron spectrum changes shape deeper into the slab. This effect is characteristic of the sensitivity of the group cross sections in the wings of a strong resonance to the averaging flux spectrum. The observed effect is not shown by the 1DF calculation because the broad group cross sections were taken there as a constant in each region. The difficulty of using constant group cross sections in regions where the spectrum is changing very rapidly has been encountered by others ⁽²²⁾.

The experimental information affords some comment on the re-entrant hole perturbation. The effect of the reentrant hole is expected to be most pronounced at the interface in energy group 7 because there are few downscattered neutrons in this energy group. The removal of the

polyethylene in creating the reentrant hole therefore removes some of the neutron source at this point. Since the measured flux at this point and energy is not much lower than the calculated value, the reentrant hole perturbation would therefore appear to be small.

It was desired to use the code GAROL to compare to experiment, but this was not possible because no position-dependent scalar fluxes were measured which could be spatially integrated for comparison to the predictions of this code. In addition, GAROL can be used only to calculate the volume averaged scalar flux in each region of an infinite lattice array, while we have merely a single cell. Nevertheless, we wanted to check some of the assumptions in GAROL that make it a very fast code, and we wished to take advantage of its greater energy detail. This was done by comparing the GAROL predictions to 1DF results which in turn were compared to experimental data.

The code GAROL computes for several hundred energies the average flux in two adjacent media by solving the coupled integral equations for the flux in each region. These equations include external and slowing down sources, and account for the transfer of neutrons between both media by means of their collision escape probabilities. A space-independent source is assumed in each region for the calculation of these collision escape probabilities. The code GAROL does not permit external leakage and all these limitations were examined before applying the code to the calculation of our problem. In Fig. 6, the 1DF calculations show that the flux in the borated polyethylene is surprisingly flat, so that the flat source assumption in GAROL is not an unreasonable approximation for the polyethylene. The observed episcadmium flux in the depleted uranium is fairly constant so that the flat source approximation is satisfactory in that medium. Consequently we are concerned only with the effect on the GAROL calculation of the leakage normal to the slabs. (We disregard the small leakage perpendicular to that direction which was

discussed earlier). The leakage in our finite geometry can be crudely approximated as the leakage from a borated polyethylene medium having the same over-all dimensions and characterized by a fundamental mode distribution. This gives a buckling B^2 , which permits us to compare the leakage $D(E) B^2$ to the absorption $\Sigma a(E)$ in the uranium. For energy groups 3 to 8, the ratio of leakage to absorption is less than 7%. Thus, only outside this energy range would leakage effects be expected to change the values of the GAROL flux computations.

The polyethylene in our system is very strongly poisoned so that the flux in the uranium will be insensitive to the effects of finite external boundaries. This has been examined by comparing two GAROL calculations, one for an infinite lattice of alternate uranium and polyethylene slabs identical to those in our geometry, and the other for a lattice in which the polyethylene slabs were taken to be 250 cms thick (the width of the uranium slabs still being 3.14 cms). The ratio of the average flux in the uranium for the second case to the first case was found to be different by at most 9.5%, thus indicating an insensitivity of the average flux in the uranium to neutron events beyond 2.5 cms of the borated polyethylene. It has thus been possible to correct the GAROL flux computations and apply them to our finite geometry by assuming that the change per unit lethargy of the flux ratio for the two lattice calculations at the 6.68 eV resonance energy provides a measure of the leakage in the uranium. This approach is based on the fact that at 6.68 eV the vacuum boundary conditions of the actual system are matched by those of the infinite lattice calculation. We have used this measure of the leakage effect to correct the GAROL computations: other details of the correction procedure are given in Ref. 23.

The fluxes computed by GAROL are shown in Fig. 10. The effect of the finite geometry on the spectrum is seen to be small. The GAROL-calculated average scalar flux in the uranium shows the presence of the

Figure 10. Region averaged fluxes calculated with GAROL.

^{235}U resonances that were observed in the measured data but could not be calculated by 1DF due to the limitations of the broad energy group structure used.

In Fig. 11, we compare the GAROL and 1DF fluxes as normalized in energy Group 1 (11.0 eV to 9.0 eV). For the sake of presenting them in a comparable fashion, the former have been averaged in energy within each 1DF broad group, and the latter have been averaged in each material region. The agreement of GAROL with 1DF, and thus indirectly with experiment, is good, the maximum difference over the entire energy range being only 7%. It is possible that this difference could have been reduced if more energy groups could have been used in the 1DF calculations. The coincidence of the flux dip at the resonance energy is remarkable. It would appear that the average scalar spectrum in the resonance absorber in systems similar to ours can be calculated reasonably well with GAROL and with much more energy detail than with 1DF. In addition, the agreement between 1DF and GAROL when such greatly different methods are used in each code lends confidence to the adequacy of the approximations in each code, those in GAROL being much more severe.

4. CONCLUSIONS

Spatially dependent neutron spectra have been measured in the resolved resonance energy region in a slab system of depleted uranium and borated polyethylene with very good spatial and energy resolution. The measurements have demonstrated that time-of-flight techniques are suitable for making detailed observations of the resonance flux in such heterogeneous systems. Spectral calculations have been performed in the neighborhood of the 6.68 eV resonance in ^{238}U separately with high spatial and energy resolution. The agreement of measurements with theory and the self-consistency of the calculations lends confidence to the nuclear cross sections used and to the ability of the codes which were used to account for flux variations in strongly anisotropic situations.

Figure 11. Comparison of the GAROL and 1DF calculated fluxes in the uranium and borated polyethylene regions.

The studies have shown that careful analysis of the background is necessary to obtain a reasonable description of the flux at the resonance energies. In addition, little indication of reentrant hole perturbation has been found. The different S_n transport theory calculations performed with 1DF have shown surprisingly small dependence on the order of quadrature n . Some sensitivity to the weighting flux used to get the group cross sections in the resonance wings was observed. The spatial representation in 1DF was difficult and limiting. Nevertheless, no spatial or angular oscillations were observed at quite coarse meshes. It was found that the space averaged fluxes in our finite geometry could be calculated reasonably well with the infinite lattice slowing down code GAROL. The agreement of GAROL predictions with 1DF results and the agreement of the latter to the experimental data support the adequacy of the approximations in the GAROL code. Specifically, the flat source approximation for computing collision escape probabilities was found to be satisfactory even for a uranium slab as thick as 3.14 cms. Neglect of inelastic scattering was also a good assumption in this code at the 6.68 eV resonance in ^{238}U .

The experimental methods demonstrated here provide means for evaluating simplified methods for computing resonance absorption in laminated shields of homogeneous and heavy metal slabs. In addition, the methods described here may be used to check:

1. Files of resonance cross sections below a few hundred eV
2. The approximations used in reactor analysis to describe self-shielding effects.
3. The energy meshes which are necessary to account for strong resonance absorption in reactor materials.

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