INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
A Xerox Education Company
KNIRK, Dwayne Lee, 1945-
STUDIES IN SCATTERING: LIGHT SCATTERING FROM
A REACTIVE EUCLERIAN FLUID AND ELECTRON
SCATTERING FROM ATOMIC HYDROGEN.

Rice University, Ph.D., 1972
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan
RICE UNIVERSITY

STUDIES IN SCATTERING:
LIGHT SCATTERING FROM A REACTIVE EULERIAN FLUID
AND
ELECTRON SCATTERING FROM ATOMIC HYDROGEN

by

Dwayne L. Knirk

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Thesis Director's signature

Houston, Texas
May, 1972
PLEASE NOTE:

Some pages may have indistinct print.
Filmed as received.

University Microfilms, A Xerox Education Company
To my Mother and Father,

whose complete dedication to their children,
whose lifetime of care and concern,
whose patience, understanding, and encouragement, and
whose unfailing love

will always place them first in my heart, I dedicate

this thesis as a symbol of my appreciation and admiration.
ACKNOWLEDGEMENTS

The debt I owe to my friends at Rice University is a large one indeed. It is only through the combined efforts of many that this thesis has become a reality.

Professor Zevi W. Salsburg was my thesis director for Part I, and it is indirectly due to him that I came here. His patience and desire to educate were invaluable to me. I am thankful for the association I had with him. My regrets are two—that he did not see the completion of our work together, and that I was not able to continue to draw on his ideas and knowledge in these later years.

Professor Edward F. Hayes was my thesis director for Part II. The interest and enthusiasm he brought to our collaboration were a continual source of motivation. I am grateful also for our many hours of discussion which helped to give me needed perspective. I hope the example I may set for others will be as good as the one he has set for me.

For the many divertissements which he provided, both academic and intellectual, Professor John E. Kilpatrick is well remembered.

I have been fortunate to have shared offices with Drs. Lannie Casey and Allen White. Our many discussions—some heated, some informative, but all interesting—made the workday a good deal more enjoyable, and definitely increased my awareness of both scientific and non-scientific matters. I have derived benefits also from Dr. Albert Siu and Kurt Alex.

I wish to acknowledge especially my friendship with Dr. James Gole, without whom my graduate career would most certainly have been a different one. Though often hidden by our humorous verbal jousting, a firm mutual
respect has developed between us, and I am pleased we were able to share our experiences here.

To Mrs. Dorothy Butler is due a generous portion of sincere gratitude. She remained imperturbable and indefatigable in the face of my most trying demands on her skills—nearly illegible manuscripts, last minute changes, and a multitude of fussy corrections. Her pleasant manner and good nature have added delightfully to the high quality of her work. Thanks goes also to Mrs. Jill Ward for the fine work she did on the many tables.

I would like to thank the National Science Foundation for the two years of predoctoral fellowship support which they provided.

Finally, I wish to acknowledge the most special source of inspiration and optimism for this thesis, a wellspring of encouragement as well as affection, my fiancée, Dot.

This research has been supported by grants to Rice University from the National Science Foundation, the Robert A. Welch Foundation, and the National Institutes of Health.
INTRODUCTION

This thesis contains accounts of two scattering studies. The first one aims to describe the spectrum of polarized light which has been scattered from a reactive fluid in terms of the thermodynamic and hydrodynamic properties of that fluid, particularly those related to the reaction. The second one aims to calculate partial wave cross sections for the scattering of an electron by a hydrogen atom. These are referred to as LS (Light Scattering) and ES (Electron Scattering) respectively.

Despite their fundamental differences, these studies have several superficial similarities. First, the basic scattering formalism is already well known. For LS, the standard method is to consider the scattered wave as radiation from a time-dependent dipole induced by the incident wave. The properties of the dipole are then described by the equations of non-equilibrium thermodynamics, and the solution of these equations can be used to describe the scattered light spectrum in terms of the parameters of the fluid. For ES of the type studied here, the close coupling method from quantum mechanical scattering theory has been standard. It assumes that the perturbed hydrogen atom can be described by only a few of its stationary states, and considers only low total angular momentum states.
Further similarities exist. Both studies focus on the implementation of the standard approaches by using recently developed techniques; these are the matrix eigenvalue technique for LS and the noniterative integral equation technique for ES. Both problems have been the subject of much investigation in recent years, and the common goal of the present studies is to compare the new techniques with previous ones. No comparison with experimental results is attempted.

The actual studies are very different in both concept and execution. LS is a macroscopic problem concerned with the collective behavior of particles in a fluid. It assumes a simple description of the scattering process and uses classical continuum equations to describe the fluid. Approximate analytical solutions of these equations are obtained and used to construct expressions for spectral characteristics. These expressions depend explicitly on the material parameters for the fluid, and can be used to determine certain reaction parameters from experimental spectra.

ES, on the other hand, is a microscopic two-body problem dealing with the scattering process itself, and the system requires a full quantum mechanical treatment for its description. The sets of coupled equations describing the scattering are integrated numerically to obtain the solutions and desired cross sections. The modification of the noniterative integral equation technique to treat a problem in which electron exchange terms are included is of as much importance as the actual numerical results.
TABLE OF CONTENTS

PART I
LIGHT SCATTERING FROM A REACTIVE EULERIAN FLUID

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CHAPTER ONE. INTRODUCTION TO LIGHT SCATTERING</td>
<td>1</td>
</tr>
<tr>
<td>1.</td>
<td>General Theoretical Approaches</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Phenomenological Theory of Light Scattering</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Molecular Theory of Light Scattering</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>Methodology</td>
<td>16</td>
</tr>
<tr>
<td>3.</td>
<td>Related Studies</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Appendix</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>CHAPTER TWO. LIGHT SCATTERING FROM THE CHEMICALLY REACTIVE EULERIAN FLUID</td>
<td>44</td>
</tr>
<tr>
<td>1.</td>
<td>Introduction</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Comments on Perturbation Methods</td>
<td>47</td>
</tr>
<tr>
<td>2.</td>
<td>Light Scattering Formalism</td>
<td>48</td>
</tr>
<tr>
<td>3.</td>
<td>Eulerian Fluid Model</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Outline of the Formal Solution</td>
<td>51</td>
</tr>
<tr>
<td>4.</td>
<td>Hydrodynamic Analysis</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Fluctuation Theory</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>The Matrix M</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>One Reaction Case</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Eigenvalue Problem</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>The Hydrodynamic Modes</td>
<td>63</td>
</tr>
</tbody>
</table>
PART II

ELECTRON SCATTERING FROM ATOMIC HYDROGEN

CHAPTER ONE. INTRODUCTION TO QUANTUM MECHANICS OF

PARTICLE SCATTERING

1. Simple Elastic Scattering

The Scattering Process 134
Free Waves 135
Scattered Waves and Cross Sections 140
Partial Wave Analysis 143
Green Functions and Scattering 150

2. Multichannel Scattering

Scattering Process, Cross Sections, and Coupled Equations 159
Extended Partial Wave Analysis 164
Green Function for the Multichannel Case 167
Close Coupled Approximation 169

3. Electron-Hydrogen Atom Scattering

Coupled Basis 174
Relation Between Coupled and Uncoupled Representations and the Radial Equations 176
Spin Coupling and Exchange 181

References 185
CHAPTER TWO. CLOSE COUPLED CALCULATIONS OF ELECTRON-HYDROGEN
ATOM SCATTERING USING A NONITERATIVE INTEGRAL EQUATION

TECHNIQUE

1. Theory
   Partial Wave Analysis
   Noniterative Integral Equation Development
   Calculation of the R Matrix

2. Computational Aspects

3. Numerical Results and Discussion
   Single Channel Phase Shifts
   1s-2s Strong Coupling Calculations
   1s-2s-2p Close Coupling Calculations

4. Summary and Conclusions

Appendix
References
Tables

CHAPTER THREE. METHOD FOR TREATING LONG RANGE INTERACTIONS IN
NONITERATIVE INTEGRAL EQUATION FORMALISM

1. Theory

2. Application to Electron-Hydrogen Atom System

3. Results for Electron-Hydrogen Atom System

4. Conclusions

Appendix
References
Tables
CHAPTER FOUR. NUMERICAL STUDIES AND COMPUTATIONAL PROCEDURES 247

1. Trapezoidal Rule Algorithm 248

2. Convergence Studies and Detailed Results 256
   
   One Channel Calculations. The 1s Exchange Approximation 257
   
   Two Channel Calculations. The 1s-2s Exchange Approximation 261
   
   Three and Four Channel Calculations. The 1s-2s-2p Exchange Approximation 264

3. Computer Algorithms and Program 277
   
   Algorithms for Required Constants and Functions 277
   
   FORTRAN Computer Program 290

Figure 1 291

References 296

Appendix 297

Tables 327
CHAPTER ONE
PART I

LIGHT SCATTERING FROM A REACTIVE EULERIAN FLUID
CHAPTER ONE. INTRODUCTION TO LIGHT SCATTERING

This chapter does not intend to give a detailed or comprehensive discussion of light scattering from liquids. Rather, it outlines the theoretical approaches to the problem and some of the applications which have been made. Thorough accounts of the theory and practice of light scattering through the mid-1960's may be found in the review article\(^1\) and book\(^2\) by I. L. Fabelinskii. Additional useful discussions of scattering by liquids are contained in the book\(^3\) edited by Temperly, Rowlinson, and Rushbrooke.

1. GENERAL THEORETICAL APPROACHES

The theoretical calculation of light scattering by a macroscopic system requires a consideration of two problems. The scattering volume is treated as a collection of scattering elements. The scattering due to each element is calculated by an application of electromagnetic theory, and contributions from each element are then combined according to some statistical theory to yield the net scattering by the system. The two approaches to be discussed here differ primarily in their choice of the "scattering element". Both approaches, however, make use of the following basic description of the scattering process.

Consider a small element of matter of volume \( V^* \) at the origin, whose dimensions are much less than those of light, and which is characterized by \( \alpha \), the polarizability per unit volume. A light wave \( \vec{E}_o \) incident upon \( V^* \) is assumed to have the form

\[
E_o(r,t) = \varepsilon_o \exp[i(k_o \cdot r - \omega_o t)],
\]  

(1.1)
where $\mathbf{e}_o$ is a constant vector (the polarization), $\mathbf{k}_o$ is the propagation vector of the wave, and $\omega_o$ is its angular frequency. This wave will induce a time-dependent dipole in $V^*$ according to

$$
P(t) = \alpha V^* E_o(0,t) = \frac{\varepsilon - 1}{4\pi} V^* E_o(0,t)
$$

(1.2)

The dielectric constant per unit volume in $V^*$ is $\varepsilon$. The use of scalars for $\alpha$ and $\varepsilon$ restricts the application of this theory to only the polarized part of an incident light wave; thus, the polarization $\mathbf{P}$ lies along $\mathbf{e}_o$. This time-dependent dipole emits a secondary radiation field whose magnitude at $R$ is

$$
|E_s(R,t)| = \frac{1}{c R} [\dot{P}(t')] \sin \phi
$$

(1.3)

where $c$ is the speed of light, $R$ is the distance from the element to the point of observation, $\phi$ is the angle between $E_o$ and $R$, and the dot notation for time derivatives is used. The square brackets indicate evaluation at the retarded time $t' = t - R/c$. The intensity of the scattered wave follows from

$$
I_s(R,t) = \frac{c}{4\pi} |E_s(R,t)|^2 = I_o \frac{k o^2 V^2}{R^2} \frac{2}{\alpha \sin^2 \phi}.
$$

(1.4)

This simple description of dipole radiation may be found in Marion.\textsuperscript{4}
Phenomenological Theory of Light Scattering

The phenomenological theory is primarily a thermodynamic approach. The scattering elements are the "small volume elements" which are so popular in nonequilibrium thermodynamics. They are small enough that the light wave is essentially constant throughout their extent, but large enough that a dielectric constant, as well as entropy, pressure, and other thermodynamic properties may be defined. Typically, the volume element can be considered a cube of side about 250 Å. For common liquids, the average number of molecules in this element is on the order of $10^4$.

Scattering from the volume element is due to fluctuations of the dielectric constant. To see why this is so, it is sufficient to note that if the dielectric constant were to truly be a constant $\varepsilon_0$ throughout the sample, every element would scatter the same and in a definite phase relationship with the other elements. To find the intensity of such coherently scattered light, the amplitudes from each element would have to be summed and the result squared. But for any element $V^*$, at a distance $R_1$ from the detector, it will be possible to find a $V_2^*$ at a distance $R_2$ such that $|R_1 - R_2|$ is an odd number of half-wavelengths, and the amplitudes of the scattering by each element will cancel. Extending this argument shows that there will be no net scattering observable from a macroscopic system which is truly homogeneous.

However, if there are fluctuations $\Delta \varepsilon$ which occur in the elements, then there will be an additional polarization

$$\Delta P = \frac{\Delta \varepsilon}{4\pi} V^* \frac{E}{\varepsilon_0}$$  \hspace{1cm} (1.5)
in addition to the one defined by

\[ P_{\omega} = \frac{\varepsilon_{\omega} - 1}{4\pi} \Omega \mathbf{v}^2 \mathbf{E}_{\omega}. \]

The intensity of radiation due to \( \Delta P \) is

\[ I_{V^*} = I_o \frac{k_o^4 V^*^2}{R^2} \frac{\Delta \varepsilon^2}{16\pi} \sin^2 \phi \quad (1.6) \]

where \( \Delta \varepsilon^2 \) is the mean square fluctuation of \( \Delta \varepsilon \) in \( V^* \). Now, the range of correlation of fluctuations may be on the order of 10 Å, so fluctuations in different volume elements may be considered to be completely independent; i.e., the light is incoherently scattered and the intensity given by the sum of the intensities from each element. This just amounts to a multiplication by \( V/V^* \), where \( V \) is the volume of the whole system.

The final intensity expression is

\[ I_V = I_o \frac{k_o^4 V V^*}{R^2} \frac{\Delta \varepsilon^2}{16\pi} \sin^2 \phi \quad (1.7) \]

A calculation of the intensity of scattered light is thus reduced to calculating \( \Delta \varepsilon^2 \) in terms of thermodynamic properties.

In the thermodynamic approach, \( \varepsilon \) is regarded as a function of the local non-equilibrium thermodynamic state. Thus, for simple fluids, \( \varepsilon = \varepsilon(\rho, T) \). Furthermore, this function is assumed to be the same as the one which would be defined by macroscopic equilibrium measurements. Fluctuations in \( \varepsilon \) are then calculated from

\[ \Delta \varepsilon = \frac{\partial \varepsilon}{\partial \rho} \Delta \rho \quad (1.8) \]
The temperature-dependent contribution is usually small enough to be neglected. Simple statistical thermodynamical calculation then gives

\[
\overline{(\Delta \varepsilon)^2} = \overline{(\frac{\partial \varepsilon}{\partial \rho})^2 \Delta \rho^2} = \left( \rho \frac{\partial \varepsilon}{\partial \rho} \right)^2 \frac{k_B \beta_T}{V^*} \tag{1.9}
\]

where \( k_B \) is Boltzmann's constant and \( \beta_T \) is the isothermal compressibility. Thus,

\[
I_V = I_0 \left( \frac{k_0}{4\pi R} \right)^2 V \left( \rho \frac{\partial \varepsilon}{\partial \rho} \right)^2 k_B \beta_T \sin^2 \phi \tag{1.10}
\]

and it is seen that this does not depend on \( V^* \).

For earlier experiments, the theory just outlined was adequate for the interpretation of the observed scattering. This approach can be called "static" because it takes no cognizance of the space and time dependence of the fluctuations. Since the total intensity is insensitive to this, a simple calculation of the mean square fluctuation in \( \varepsilon \) is all that is required.

However, the spatial and temporal dependence of the fluctuations will impose a certain angular and spectral structure on the scattered light. Fluctuations are continually being generated by the random molecular motions in \( V \) and then dissipate in some complicated way. Each of the kinetic processes involved in the dissipation leaves its own particular imprint on the distribution of spectral intensities. A detailed study of this spectral structure can thus be used to elucidate the kinetic processes in the fluid. An important point is that this method of observation causes essentially no perturbation of the system.
The theory appropriate for this type of analysis can be called the "dynamic" phenomenological theory. Since this is the basis of the calculation in Chapter 2, it will be presented in some detail.

A straightforward calculation can be done to see exactly how the space and time dependence of the fluctuations affects the scattered light. Again, the total volume \( V \) is assumed to be composed of small elements \( V^k \). Each element is large enough to be considered as an ensemble with well defined thermodynamic properties and which can be assigned a dielectric constant, \( \varepsilon \). Each element is small enough, however, that on a macroscopic (light wave dimensions) scale, it is essentially a point. Thus, the dielectric constant for \( V \) can be expressed as

\[
\varepsilon(r,t) = \varepsilon_0 + \Delta\varepsilon(r,t) \quad (1.11)
\]

where \( \varepsilon_0 \) is the average dielectric constant and \( \Delta\varepsilon(r,t) \) is the fluctuation in \( \varepsilon \) occurring in the volume element surrounding \( r \). Because of preceding comments, \( \varepsilon(r,t) \) is regarded as a continuous function of \( r \).

As before, an incident wave of the form

\[
E_0(r,t) = \varepsilon_0 \exp[i(k_0 \cdot r - \omega_0 t)] \quad (1.12)
\]

incident upon \( V \) induces a polarization along \( \varepsilon_0 \)

\[
\varepsilon_0 P(r,t) = \varepsilon_0 \frac{\Delta\varepsilon(r,t)}{4\pi} \exp[i(k_0 \cdot r - \omega_0 t)] \quad (1.13)
\]

since it can be shown that the contribution from \( \varepsilon_0 \) is a scattered wave along \( k_0 \). Defining the Hertz vector \( Z(R,t) \) as the solution of
\[
\n\nabla^2 Z(R,t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} Z(R,t) = -4\pi \varepsilon_0 P(R,t) \tag{1.14}
\]

the resulting electric field \(E_s(R,t)\) is determined by

\[
E_s(R,t) = \nabla(\nabla \cdot Z) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} Z. \tag{1.15}
\]

The solution for \(Z\) is easily given in terms of the retarded Green's function:

\[
Z(R,t) = \int d^3r \int dt' \varepsilon_0 \frac{P(r,t')}{|R-r|} \delta(t' - t + |R-r|/c). \tag{1.16}
\]

Performing the operations indicated in (1.15) results in the following expression for \(E_s\) in the radiation zone.

\[
E_s(R,t) = \xi (c^2 R)^{-1}
\]

\[
\times \int d^3r \int dt' \left[ \left( \frac{\partial}{\partial t'} \right)^2 P(r,t') \right] \delta(t' - t + |R-r|/c) \tag{1.17}
\]

where \(\xi\) lies in the plane of \(\varepsilon_0\) and \(R\) and is given by

\[
\xi = \varepsilon_0 - (\varepsilon_0 \cdot R)R/R. \tag{1.18}
\]
It is easily seen that $|\xi|^2 = |e_o|^2 \sin^2 \phi$, where $\phi$ is the angle between $e_o$ and $R$.

The delta function is next expanded as a Fourier integral. Since the observation point $R$ is assumed to lie far outside the scattering volume, then

$$|R - \mathbf{r}| \approx R - R \cdot \mathbf{r}/R \quad (1.19)$$

where $R = |R|$. Discarding terms of $O(r/R)$, the scattered field is given by

$$E_s(R, t) = \xi (8\pi^2 c^2 R)^{-1} \int d^3 r \int dt' \int d\omega' e^{ik \cdot r} \int d^3 r' \Delta e(r, t, r') e^{-i\omega t'} \quad (1.20)$$

Now, the vector defined by

$$k_s \equiv \omega' R/cR \quad (1.21)$$

is just the propagation vector at the point of observation for scattered light of frequency $\omega'$.

Also, since $k_s$ is parallel to $R$,

$$k_s \cdot R = \omega' R/c = k_s R \quad (1.22)$$
The scattered field may be expressed as

\[ E_s(R, t) = \xi (8\pi^2 c^2 R)^{-1} e^{ik_s R} \int d^3 r \int dt' e^{ik' r} \]

\[ \times \int d\omega' \exp[i\omega'(t' - t)] \left[ \left( \frac{\partial}{\partial t'} \right)^2 \Delta \varepsilon(r, t') e^{-i\omega_o t'} \right] \]

\[ = \xi (4\pi c^2 R)^{-1} e^{ik_s R} \int d^3 r e^{-i\omega t} \left[ \left( \frac{\partial}{\partial t} \right)^2 \Delta \varepsilon(r, t) e^{-i\omega_o t} \right] , \]

(1.23)

where the integral over \( \omega' \) was evaluated first to give \( 2\pi \delta(t - t') \),

and \( k = k_o - k_s \). The following assumption is now made. 6

Consider the temporal character of the dissipative processes which

will determine the time dependence of \( \Delta \varepsilon \). Their relaxation probably

occurs slowly compared to the frequency of light. Hence,

\[ \frac{\partial^2}{\partial t^2} \Delta \varepsilon(r, t) e^{-i\omega_o t} = -\omega_o^2 \Delta \varepsilon(r, t) e^{-i\omega_o t} . \]

(1.24)

The final expression for the scattered field is then

\[ E_s(R, t) = -\xi \frac{k_o^2}{4\pi R} e^{ik_s R} e^{-i\omega_o t} \]

\[ \times \int d^3 r e^{-i\omega t} \Delta \varepsilon(r, t) . \]

(1.25)
The spectral intensity may be defined

\[
I(R, k, \omega_s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{i\omega_s t} \langle E_s^*(R, t') \cdot \overline{E_s(R, t' + t)} \rangle
\]

\[
= \frac{1}{\pi} \text{Re} \int_{0}^{\infty} dt \ e^{i\omega t} \langle E_s^*(R, t') \cdot \overline{E_s(R, t' + t)} \rangle ,
\]

(1.26)

where the angular brackets denote an ensemble average. The second equality results from the assumption that

\[
\langle \Delta \varepsilon(-k, t' - t) \Delta \varepsilon(k, t') \rangle = \langle \Delta \varepsilon(-k, t') \Delta \varepsilon(k, t' + t) \rangle ;
\]
i.e., the correlation function is stationary in time. This allows \( t' \) to be set to zero. Using the expression for \( E_s \) results in the following expression for the scattered intensity:

\[
I(R, k, \omega) = I_o \left( \frac{k_o^2}{4\pi R} \right)^2 \sin^2 \frac{2\phi}{2\pi}
\]

\[
\times 2 \text{Re} \langle \int d^3 r' \ dt \ \exp(-ik \cdot r'') \Delta \varepsilon(r'', o) \rangle
\]

\[
\times \int d^3 r' \int dt \ \exp[i(k \cdot r - \omega t)] \Delta \varepsilon(r', t) \rangle ,
\]

(1.27)

where \( \omega = \omega_s - \omega \) and \( I_o \) is the intensity of incident radiation. In the literature, this equation is often found expressed in terms of the spatial Fourier transforms of the density fluctuations,

\[
\Delta \rho(k, t) = \int d^3 r \ e^{ik \cdot r} \left[ \rho(r, t) - \rho_o \right]
\]

(1.28)
as

\[
I(R, k, \omega) = I_o \left( \frac{k_o^2}{R} \right)^2 \sin^2 \frac{2\phi}{2\pi}
\]

\[
\times \int dt \ e^{-i\omega t} \langle \Delta \rho(-k, o) \Delta \rho(k, t) \rangle .
\]

(1.29)
The quantity $\alpha$ can be regarded as an effective polarizability per particle, so that

$$\Delta \varepsilon = \frac{\partial \varepsilon}{\partial p} \Delta p = (4\pi \alpha) \Delta \rho$$

(1.30)

As in the static theory, the temperature dependence of $\varepsilon$ is neglected. Since $\omega/\omega_0$ is always much less than unity, the light is quasi-elastically scattered,

$$|k_s| \approx |k_o|$$

(1.31)

and $k = |k_o - k_s|$ becomes a parameter of the apparatus configuration, namely,

$$k = 2 k_o \sin \frac{\theta}{2}$$

(1.32)

where $\theta$ is the angle of scattering.

Either of the equations, (1.27) or (1.29), forms the basis of the dynamic phenomenological theory of light scattering. For any particular application, all that is necessary is to compute the spatial and temporal transforms of $\Delta \varepsilon(r,t)$, an operation more easily stated than performed. To do this in the context of thermodynamics, Eq. (1.29) may be used as it stands, or (1.27) may be used and full dependence of $\varepsilon$ on the local thermodynamic state taken into account by

$$\Delta \varepsilon(r,t) = \frac{\partial \varepsilon}{\partial p} \Delta p(r,t) + \frac{\partial \varepsilon}{\partial s} \Delta s(r,t) + \cdots$$

(1.33)
The relevant kinetic theory is then used to calculate the space-time dependence of the fluctuations of the thermodynamic quantities. Once more, the coefficients \( \partial \varepsilon / \partial \rho \), etc., are taken to have their macroscopic equilibrium values.

Molecular Theory of Light Scattering

Nevertheless, it is true that any phenomenological theory overlooks many aspects of the system to which it is applied. Hence, it is desirable to formulate a detailed molecular theory which, in principle, would provide the possibility of obtaining detailed information on the molecular structure of the system from experimental data on the intensity and spectral composition of the scattered light.

Such a theory was developed by Van Hove\(^7\) for describing slow-neutron scattering. The actual scattering by each center was described by the Born approximation, and the effects of the distribution of scattering centers were contained in a space-time correlation function, \( G(\mathbf{r},t) \), a time-dependent generalization of the ordinary radial distribution function \( g(\mathbf{r}) \). This correlation function was defined in terms of the ensemble average of a function of the Heisenberg operators

\[
\hat{r}_j(t) = e^{i t \mathbf{H} \hat{\mathbf{r}} / \hbar} \hat{r}_j e^{-i t \mathbf{H} \hat{\mathbf{r}} / \hbar}
\]
where \( r_j \) is the position operator of the \( j \)-th scattering center and \( H \) is the Hamiltonian of the system.

Van Hove's theory was "translated" into the language of light scattering by Komarov and Fisher. The starting point for their analysis is the molecular equivalent of Eq. (1.13),

\[
P(\tilde{r}, t) = E_0(\tilde{r}, t) \sum_{i=1}^{N} \alpha \delta(\tilde{r} - \tilde{r}_i(t))
\]  

(1.34)

where \( \alpha \) is a mean polarizability per molecule, \( \tilde{r}_i(t) \) is the position of the \( i \)-th molecule, and there are \( N \) molecules in the system. Following the same arguments as before, the intensity is found to be

\[
I(R, k, \omega) = I_0 \left( \frac{k^2 \alpha}{2R} \right) \frac{\sin^2 \phi}{2\pi} \int dt \ e^{-i\omega t} \\
\times \int d^3 r' \int d^3 r'' \left\langle \sum_{i,j} e^{-ik \cdot r''} \delta(\tilde{r}'' - \tilde{r}_i(0)) e^{ik \cdot r'} \delta(\tilde{r}' - \tilde{r}_j(t)) \right\rangle.
\]

(1.35)

Performing the volume integrals gives

\[
I(R, k, \omega) = I_0 \left( \frac{k^2 \alpha}{2R} \right) \frac{\sin^2 \phi}{2\pi} \\
\times \int dt \ e^{-i\omega t} \left\langle \sum_{i,j} \exp[-i k \cdot (\tilde{r}_i(0) - \tilde{r}_j(t))] \right\rangle.
\]

(1.36)
The significance of the expression in angular brackets is that it is a time-dependent generalization of the familiar Bragg scattering law.

Now, Van Hove defined the pair distribution function by

\[ G(\mathbf{r}, t) = \left( \frac{1}{2\pi} \right)^3 N^{-1} \times \int d^3k \ e^{-i\mathbf{k} \cdot \mathbf{r}} \left\langle \sum_{i,j} \exp[-i\mathbf{k} \cdot (\mathbf{R}_i(0) - \mathbf{R}_j(t))] \right\rangle. \]  

(1.37)

Thus, the spectral intensity of scattered light may be described by the formula

\[ I(R, k, \omega) = I_0 N \left( \frac{k_o^2 \alpha}{R} \right)^2 \frac{\sin \phi}{2\pi} \times \int d^3r \int dt \ e^{i(k \cdot r - \omega t)} G(\mathbf{r}, t). \]  

(1.38)

The properties and significance of \( G(\mathbf{r}, t) \) are discussed in considerable length in the original paper. In particular, the asymptotic form for large \( |\mathbf{r}| \) or large \( |t| \) is

\[ G(\mathbf{r}, t) \sim N^{-1} \int d^3r' \ \rho(\mathbf{r}' - \mathbf{r}) \rho(\mathbf{r}') \]

(1.39)

which is the autocorrelated density function. The density, defined in this context by

\[ \rho(\mathbf{r}) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i(t)) \right\rangle \]

(1.40)
is just the average density of the system, which is independent of $t$.
In a homogeneous system

$$G(r,t) \sim \rho_0.$$  \hspace{1cm} (1.41)

It is easy to see from Eq. (1.38) that this part of $G$ gives just the elastic scattering in the forward direction, which of course is indistinguishable from the incident radiation. The distinct part of the intensity can then be written

$$I(R, k, \omega) = I_0 N \left( \frac{k_o^2 \alpha}{R} \right)^2 \frac{\sin^2 \phi}{2\pi}$$

$$\times \int d^3r \int dt \, e^{i(k \cdot \xi - \omega t)} \left[ G(r,t) - \rho_0 \right].$$  \hspace{1cm} (1.42)

Once again, the problem of computing the spectral intensity of scattered light is reduced to a calculation of the space and time dependence of the behavior of fluctuations in the system. For the study of simple fluids, it is seen that the phenomenological theory or the molecular theory supplies essentially the same link between fluctuations in the system and the scattered intensity. Being far more fundamental in approach, however, the molecular theory has application to such problems as the analysis of rotational relaxation of molecules in solution, the determination of long wavelength normal modes of polymers, and the like. A consideration of such studies is beyond the scope of the present discussion. A difficulty is that this form is not easily extended to systems of more than one component.
2. METHODOLOGY

Section 1 of this chapter demonstrated the connection between
the spectral intensity of light scattered from a fluid and the space
and time dependence of fluctuations occurring in that fluid. In this
section, a model calculation for a simple pure fluid will be performed
which illustrates most of the features of a scattered light spectrum.
The intent of this calculation is to provide the reader with a suffi-
ciently clear understanding of the methods used and the results obtained,
that the current literature may be more easily understood. Again, the
book by Fabelinskii\(^9\) discusses many of the physical ideas and history
involved in the development of these calculations. In particular, his
notation and thermodynamic relations will be used for the present dis-
cussion. Since Eq. (1.27) is the starting point for Chapter Two, it
will also be used here.

Now, by invoking the assumption of local thermodynamic equilibrium,
and then choosing a set of variables, \(x_i\), to describe the local state,
the fluctuations in \(\varepsilon\) may be computed from

\[
\Delta\varepsilon(\tau, t) = \sum_i \left( \frac{\partial \varepsilon}{\partial x_i} \right)_0 \Delta x_i(\tau, t),
\]

(2.1)

where the superscript zero means that the macroscopic equilibrium value
of these derivatives will be used. It is desired to compute the
"structure factor"

\[
S(\kappa, \omega) = 2 \text{Re} \int_0^\infty dt \, e^{-i\omega t} \langle \Delta\varepsilon(-\kappa, 0)\Delta\varepsilon(\kappa, t) \rangle,
\]

(2.2)
where

$$
\Delta \varepsilon(k, t) = \int d^3 r \ e^{i k \cdot r} \ \Delta \varepsilon(r, t) = \sum_i \left( \frac{\partial \varepsilon}{\partial x_i} \right)^0 \Delta x_i(k, t)
$$

(2.3)

The calculation of $S(k, \omega)$ involves two distinct problems. First, the time evolution of the Fourier modes of the $\Delta x_i$ must be determined so that $\Delta x_i(k, t)$ may be expressed in terms of its "initial value", $\Delta x_i(k, 0)$. This is usually accomplished by solving a set of hydrodynamic equations which have been linearized to describe small displacements from the equilibrium state of the system. The solution of this problem determines the spectral distribution of the intensity.

The second problem is the calculation of the ensemble averages $\langle \Delta x_i(-k, 0) \Delta x_j(k, 0) \rangle$, or equivalently, $\langle \Delta x_i(r, 0) \Delta x_j(r', 0) \rangle$. This determines the actual magnitude of the intensity distribution. Since correlations normally extend for only a short range, $R_c$, compared with the wavelength of light, this can be reduced to a calculation of $\langle \Delta x_i \Delta x_j \rangle$ in a volume element $V_c \approx R_c^3$. The necessary average values are calculated by ordinary statistical mechanics.

For the model calculation, the pressure $p$ and entropy $S$ will be taken as the variables to describe the system, so

$$
\Delta \varepsilon(k, t) = \left( \frac{\partial \varepsilon}{\partial p} \right)_S^0 \Delta p(k, t) + \left( \frac{\partial \varepsilon}{\partial S} \right)_p^0 \Delta S(k, t)
$$

(2.4)
where $\Delta p$ and $\Delta S$ are the fluctuations in $p$ and $S$. Kinetic equations are needed in order to get the time dependence of $\Delta p$ and $\Delta S$. Now, the pressure fluctuations are regarded as a superposition of an infinite number of sound waves propagating in all directions. Thus, the appropriate "equation of motion" for $\Delta p$ is the Stokes equation for sound propagation in a viscous medium

$$\left[ \frac{\partial^2}{\partial t^2} - c_o^2 \nabla^2 - \Gamma \nabla^2 \frac{\partial}{\partial t} \right] \Delta p(\vec{r},t) = 0 \quad (2.5)$$

where $c_o$ is the sound speed and $\Gamma$ is the damping coefficient by which energy is dissipated by viscous forces and heat flow. The required equation for $\Delta S$ may be derived as follows. Consider the heat flow $\delta q$ due to fluctuations in temperature,

$$\delta q = -\kappa \nabla (\delta T)$$

where $\kappa$ is the thermal conductivity. The "diffusion" of entropy is governed by

$$\frac{\partial}{\partial t} \Delta S(\vec{r},t) = - (v/T) \nabla \cdot (\delta q)$$

$$= (v\kappa / T) \nabla^2 (\delta T)$$

where $v$ is the specific volume. At constant pressure,

$$\delta T = (T/C_p) \Delta S$$
so that the kinetic equation for $\Delta S$ has the form

$$\left[ \frac{\partial}{\partial t} - \frac{v\kappa}{C_p} \nabla^2 \right] \Delta S(\vec{r}, t) = 0 . \quad (2.6)$$

The equations for the Fourier components

$$\Delta p(k, t) = \int d^3r \ e^{ik \cdot \vec{r}} \Delta p(\vec{r}, t),$$

$$\Delta S(k, t) = \int d^3r \ e^{ik \cdot \vec{r}} \Delta S(\vec{r}, t), \quad (2.7)$$

are easily found by replacing $\nabla^2$ by $-k^2$ in Eqs. (2.5) and (2.6), giving

$$\left[ \frac{\partial^2}{\partial t^2} + c_o^2 k^2 + \Gamma k^2 \frac{\partial}{\partial t} \right] \Delta p(k, t) = 0 \quad (2.8)$$

$$\left[ \frac{\partial}{\partial t} + \chi k^2 \right] \Delta S(k, t) = 0 \quad (2.9)$$

where

$$\chi = \frac{v\kappa}{C_p} \quad (2.10)$$

is the thermal diffusivity. The vectorial designation on $k$ is omitted since it is no longer necessary. The equations are immediately solved to give
\[ \Delta p(k,t) = \exp\left[-\frac{1}{2} \Gamma k^2 t\right] \cos \Omega t \Delta p(k,0), \]  
(2.11)

\[ \Delta S(k,t) = \exp[-\chi k^2 t] \Delta S(k,0), \]  
(2.12)

where

\[ \Omega = \sqrt{\left[c_0^2 - \frac{1}{4} \Gamma^2 k^2 + \frac{1}{4} \chi^2 k^4\right]} \]  
(2.13)

is the effective frequency of the temporally damped sound waves. For reasonable values of \( k \), the second term in (2.13) can be neglected. The quantity \( \Omega \) then becomes a measure of the sound speed

\[ \Omega \approx c_0 k. \]  
(2.14)

Substitution of the expressions for \( \Delta p(k,t) \) and \( \Delta S(k,t) \) into Eq. (2.4), gives

\[ \left\langle \Delta \varepsilon(-k,0) \Delta \varepsilon(k,t) \right\rangle = \]

\[ \left(\frac{\partial \varepsilon}{\partial p}\right)_{S}^2 \left\langle \Delta p(-k,0) \Delta p(k,0) \right\rangle e^{-\Gamma k^2 t/2} \left[ e^{i\Omega t} + e^{-i\Omega t} \right] \]

\[ + \left(\frac{\partial \varepsilon}{\partial S}\right)_{p}^2 \left\langle \Delta S(-k,0) \Delta S(k,0) \right\rangle e^{-\chi k^2 t}. \]  
(2.15)

The cross-term is omitted because \( \left\langle \Delta S \Delta p \right\rangle = 0 \). The structure factor is easily constructed by application of the standard integral.

\[ \int_0^\infty dt \ e^{-i\omega t} e^{-\alpha t} = \frac{1}{\alpha + i\omega}, \ \text{Re} \alpha > 0. \]  
(2.16)
The result is

\[
S(k, \omega) = \\
\left( \frac{\partial \varepsilon}{\partial p} \right)_S \left\langle \Delta p(-k, o) \Delta p(k, o) \right\rangle \frac{\Gamma k^2/2}{(\Gamma k^2/2)^2 + (\omega - \Omega)^2} \\
+ 2 \left( \frac{\partial \varepsilon}{\partial S} \right)_p \left\langle \Delta S(-k, o) \Delta S(k, o) \right\rangle \frac{\chi k^2}{(\chi k^2)^2 + \omega^2} \\
+ \left( \frac{\partial \varepsilon}{\partial p} \right)_S \left\langle \Delta p(-k, o) \Delta p(k, o) \right\rangle \frac{\Gamma k^2/2}{(\Gamma k^2/2)^2 + (\omega + \Omega)^2}.
\]

(2.17)

This equation is basic to the understanding of light scattered from liquids. It is composed of three Lorentzian peaks: A Rayleigh peak centered around the incident frequency (\(\omega = 0\)) and the Mandelstam-Brillouin doublet centered at the shifted frequencies, \(\omega_s = \omega_0 \pm \Omega\).

In an "ideal" fluid which has \(\kappa = 0\) and \(\Gamma = 0\), it is seen that each peak would be a line of zero width. From Eqs. (2.11) and (2.12) it is seen that the entropy would be constant in time and the sound waves in the fluid would propagate without damping. The presence of dissipative processes (here thermal conduction and phonon absorption) serves to broaden the lines, and the broadening is proportional to the dissipation. Specifically, the half width of the Rayleigh peak is \(\chi k^2\), while that of the Brillouin peaks is \(\Gamma k^2/2\).
The spectral distribution associated with the pressure fluctuations is due to scattering from sound waves of equal amplitude travelling in opposite directions through the system, hence the presence of two peaks doppler-shifted to both higher and lower frequencies. Fluctuations in entropy do not propagate in the system and, therefore, do not shift the frequency of light.

In order to get the intensity of scattered light, it is necessary to evaluate

\[ \langle \Delta p(-k_0) \Delta p(k_0) \rangle = \int d^3 r'' \int d^3 r' e^{ik_0 \cdot (r' - r'')} \langle \Delta p(r'',0) \ p(r',0) \rangle \]

\[ \quad = \int d^3 r'' \int d^3 r e^{ik \cdot r} \langle \Delta p(r'',0) \Delta p(r'' + r_0) \rangle \]

(2.18)

where \( r = r' - r'' \). From the remarks made earlier in this section,

\[ \langle \Delta p(r'',0) \Delta p(r'' + r_0) \rangle = 0, \quad r > R_c \]

(2.19a)

\[ \quad = \langle |\Delta p|^2 \rangle, \quad r < R_c. \]

(2.19b)

That is, fluctuations are only correlated for a distance \( R_c \). Now for usual light sources and apparatus geometries, \( k \sim 10^5 \ cm^{-1} \). Since \( R_c \), the range of correlation, is expected to be on the order of \( 10^{-7} \ cm \), the exponent may be replaced by unity over the range for which (2.19b) holds, with the result

\[ \langle \Delta p(-k_0,0) \ p(k_0,0) \rangle = vV_c \langle |\Delta p|^2 \rangle. \]

(2.20)
The integration over \( r' \) was carried out to get the volume \( V \) by assuming \( \langle |\Delta p| \rangle \) is effectively independent of \( r' \). The volume element \( V_c \) is on the order of \( R_c^3 \). Now statistical mechanical fluctuation theory can be used to evaluate \( \langle |\Delta p| \rangle \) in the element \( V_c \),

\[
\langle |\Delta p| \rangle = \frac{k_B T}{\beta_s V_c}
\] (2.21)

where \( k_B \) is the Boltzmann constant and \( \beta_s \) is the adiabatic compressibility. Thus,

\[
\langle \Delta p(-k, \omega) \Delta p(k, \omega) \rangle = V \frac{k_B T}{\beta_s}
\] (2.22)

which is independent of \( V_c \). A similar treatment of the entropy term gives

\[
\langle \Delta S(-k, \omega) \Delta S(k, \omega) \rangle = V k_B C_p \rho
\] (2.23)

The explicit expression for the structure factor is

\[
S(k, \omega) = V k_B T \times \left\{ \left( \frac{\partial \varepsilon}{\partial p} \right)_p^2 \frac{1}{\beta_s} \left[ \frac{\Gamma k^2/2}{(\Gamma k^2/2)^2 + (\omega - \Omega)^2} + \frac{\Gamma k^2/2}{(\Gamma k^2/2)^2 + (\omega + \Omega)^2} \right] + 2 \left( \frac{\partial \varepsilon}{\partial S} \right)_p^2 \frac{C_p \rho}{T} \frac{x k^2}{(x k^2)^2 + \omega^2} \right\}
\] (2.24)
In order to consider the isentropic and isobaric scattering separately, define the two intensity functions

\[ I_{\text{MB}}(R,k,\omega) = A \left( \frac{\partial \varepsilon}{\partial p} \right)^2_s \beta_s^{-1} \]

\[ \times \left[ \frac{\Gamma}{(\omega + \Omega)^2} + \frac{\Gamma}{(\omega - \Omega)^2} \right] \]

\[ I_R(R,k,\omega) = 2A \left( \frac{\partial \varepsilon}{\partial p} \right)^2 \rho_c p \frac{\chi k^2}{T} \left( \frac{\chi k^2}{\omega^2} + \omega^2 \right) \]

where

\[ A = I_0 \left( \frac{k_o}{4\pi R} \right)^2 \frac{\sin^2 \phi}{2\pi} \frac{\chi k}{T} \]

A property of the spectrum which may be measured experimentally is the Landau-Placzek ratio

\[ J = \int_{-\infty}^{\infty} d\omega I_R(\omega) / \int_{-\infty}^{\infty} d\omega I_{\text{MB}}(\omega) \].

Inasmuch as the integral of each Lorentzian-form factor is just \( \pi^{10} \), this ratio is given by

\[ J = \frac{\beta_s \rho_c p}{T} \left[ \left( \frac{\partial \varepsilon}{\partial s} \right)^2 / \left( \frac{\partial \varepsilon}{\partial p} \right)^2_s \right] \]

If \( \varepsilon \) is considered as a function of \( p \) and \( T \), and its temperature derivative is neglected, the following thermodynamic relations hold:

\[ \left( \frac{\partial \varepsilon}{\partial p} \right)_s = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_s \left( \frac{\partial p}{\partial \rho} \right)_s = \beta_s \left( \frac{\partial \varepsilon}{\partial \rho} \right)_s \approx \beta_s \left( \frac{\partial \varepsilon}{\partial \rho} / T \right) \]

(2.29a)
\[
\left( \frac{\partial \varepsilon}{\partial S} \right)_p = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_p \left( \frac{\partial \rho}{\partial S} \right)_p = \frac{\sigma T}{C_p} \left( \frac{1}{\sigma} \frac{\partial \varepsilon}{\partial T} \right)_p \approx \frac{\sigma T}{C_p} \left( \rho \frac{\partial \varepsilon}{\partial \rho} \right)_T
\] 

(2.29b)

where \( \nu_S = (\partial V/\partial T)_p \) and \( \nu_S = -(\partial V/\partial \rho)_s \). In this approximation, the ratio of total scattering into the Rayleigh peak to total scattering into the Brillouin doublet is

\[
j \approx \frac{\sigma^2 \rho_T}{C_p \beta_S} = \gamma - 1
\] 

(2.30)

where \( \gamma = C_p/C_v \). In practice, the approximations in (2.29) are not always good and hence \( J \) may not be given by (2.30).

The relationship between spectral features and the processes occurring within the fluid are summarized as follows.

1. There are two peaks, the Mandel'stam Brillouin doublet, shifted equally to higher and lower frequencies from the incident frequency. The amount of shift is proportional to the sound speed at that frequency in the fluid.

2. Line widths are proportional to the coefficients characterizing the associated dissipation. For the Brillouin doublet, the width is \( \Gamma \varepsilon k^2 \) where \( \Gamma \) is the sound adsorption coefficient. For the thermal peak, the width is \( \kappa k^2 \), which is the rate of decay of entropy fluctuations.

3. The total intensity of light scattered into a peak is proportional to the mean square fluctuation which gives rise to the peak.

3. RELATED STUDIES

There are a number of studies which employ the strategy just outlines. Three general categories may be distinguished: detailed
analysis of pure fluids, idealized model calculations on two and three component mixtures, and detailed studies on multicomponent systems.

A study of light scattering from a simple fluid, approached through the calculation of the density-density correlation function, was carried out by Mountain. 12 Using the full set of hydrodynamic equations for mass, momentum, and energy transport, he obtained a structure factor equivalent in almost every way with the expression in (2.19). His intent was to describe critical opalescence, a phenomenon associated with long range correlations. The necessary modifications in the equations and the resulting spectrum were described. Parameters appropriate for CO$_2$ in the supercritical region were used to predict half-widths, frequency shifts, and intensities of the various peaks.

Because it ignored internal structure, the preceding calculation was only a first order approximation. Most real fluids of interest have internal degrees of freedom, such as rotational and vibrational excitations, which affect the thermodynamic and hydrodynamic properties in particular ways. These processes can be studied as well by light scattering experiments. In order to interpret such observations, Mountain did two studies in which he investigated the effects of internal modes of relaxation on the scattered light spectrum.

The first study$^{13}$ introduced an internal relaxation in the form of a frequency dependent part of the bulk viscosity, $\eta _1$. 14 This changes the spectrum in four ways. A second Rayleigh peak is produced whose half-width is proportional to $(\tau _1)^{-1}$, and is independent of $k$. 
The constant $\tau_1$ is the relaxation time associated with $\eta_1$. In addition, the Brillouin displacement has a much different $k$-dependence than that in Eq. (2.13), namely

$$
(\tau_1 \Omega)^2 = \frac{1}{2}[\tau_1^2 c_\infty^2 k^2 - 1] + \frac{1}{2}[(1 - \tau_1^2 c_\infty^2 k^2) + 4\tau_1^2 c_\infty^2 k^2]^{1/2},
$$

(3.1)

where $c_\infty$ is the infinite frequency limit of the sound speed $c_o$. A plot of $\Omega$ versus the dimensionless variable $\tau_1 c_\infty k$ has the sigmoid shape which characterizes dispersive behavior. In particular, for $\tau_1 c_\infty k << 1$, $\Omega$ reduces to $c_\infty k$, as before. However, when $\tau_1 c_\infty k >> 1$, $\Omega$ is $c_\infty k$. A more complete discussion of this phenomenon and the meaning of two sound speeds is given in Chapter Two but essentially what is involved is a comparison of the internal relaxation time $\tau_1$ with the relaxation time $(c_\infty k)^{-1}$ of the sound wave.

The presence of the extra dissipation is also noted in $\Gamma$, the Brillouin peak half-width. The additional terms due to $\eta_1$ were found to be not simply additive to the absorption term for $\eta_1 = 0$. Finally, the ratio of the integrated intensities of the Rayleigh peaks to the Brillouin peaks has a more complicated expression than given in Eq. (1.30). It reduces to $\gamma - 1$ when $\tau_1 \Omega << 1$, but for $\tau_1 \Omega >> 1$ the value increases to

$$
J = (\gamma - 1) \left[ 1 + \frac{\gamma}{\gamma - 1} \left( \frac{c_\infty^2 - c_o^2}{c_o^2} \right) \right]
$$

(3.2)

An alternative approach to including internal degrees of freedom is to adopt a progress variable description, similar to the one used
for discussing the thermodynamic energetics of reactions. That is, if 
E is the total internal energy, then

\[ dE = TdS - pdV + E_\xi \, d\xi \]  \hspace{1cm} (3.3)

where \( \xi \) is called the progress variable and \( (\partial E/\partial \xi)_{S,V} \equiv E_\xi \). To the 
hydrodynamic equations is appended a relaxation equation for the fluctuations \( \Delta \xi = \xi - \overline{\xi} \), of the form

\[ \frac{\partial \xi}{\partial t} = -\tau^{-1} \Delta \xi \]  \hspace{1cm} (3.4)

where \( \tau \) is the relaxation time for the decay of the fluctuations \( \Delta \xi \) which 
returns \( \xi \) to its equilibrium value \( \overline{\xi} \). Mountain\(^{15} \) pursued this within 
the framework of this earlier papers and compared the results obtained 
with those in\(^{13} \). For the case where the relaxation is purely structural 
(defined by \( \partial E_\xi / \partial T = 0 \)), the results are identical. Small differ-
ences were noted for pure thermal relaxation (defined by \( \partial E_\xi / \partial \rho = 0 \)).

Both of these methods of treating internal relaxation were used 
together in a study by Bhatia and Tong\(^{16} \). A frequency dependent 
shear viscosity was used, while bulk viscosity effects were accounted 
for by introducing a specific (but undefined) "ordering parameter" as 
just described. There are, therefore, two relaxation times in the 
system, and two additional Rayleigh peaks in the spectrum.

One other study deserving special mention is the one by Nichols and 
Carome\(^{17} \). Following Mountain's approach\(^{13} \), they include \( R \) different 
relaxing parts to the viscosity, giving explicit results for \( R = 1 \).
(Mountain's case) and \( R = 2 \). The reason for repeating Mountain's calculation was to include small terms which his first order calculation ignored. These give rise to a skewing of the Brillouin peaks from a strict Lorentzian form, an effect which has been observed experimentally. Using material parameters for \( \text{CCl}_4 \), they did a computer study of the half-widths and displacements. These "exact" results were complemented by detailed discussions of the physical mechanisms responsible for various features, particularly the skewing of the Brillouin peaks.

For \( R = 2 \), approximate expressions were first derived for the half-widths to see how multiple relaxation times enter the absorption factors. Computer results were again obtained, and were contrasted with the results for \( R = 1 \). It is felt that exact computer solutions are of considerable value for studying the results for a wide range of physical parameters and are a worthwhile supplement to the approximate analytical expressions usually derived.

It was mentioned earlier in this chapter that one of the attractions of light scattering studies is that the system under observation experiences negligible perturbation due to the scattering. Because of this, it seems that studies near phase boundaries, particularly the critical point, can be approached with a certain confidence that laboratory observations may closely reflect the true physical state of the system. Thus, modifications of the hydrodynamic equations to account for the peculiar behavior of the near-critical fluid may be studied by solving the modified equations and comparing the resulting intensity calculation with experiment. Mountain\(^{18} \) has published such a study. Three modifications were made. The first was the "Fixman modification", an attempt to account for long range two-body correlations. The Ornstein-Zernike correlation length \( \kappa^{-1} \) is thus introduced into the equations.
The other modifications were the inclusion of relaxations in both the bulk viscosity and thermal conductivity which have relaxation times \( \tau \) and \( \bar{\tau} \), respectively. Various aspects of the experimental spectrum of CO\(_2\) in the region \( 0.05 \leq T - T_c \leq 5 \) K were then used to develop a consistent set of values at each temperature for the parameters \( \gamma = c_p/c_v \), \( \kappa^{-1} \), \( \tau \), and \( \bar{\tau} \). It was found that \( \bar{\tau} = 0 \) allowed the predicted and observed spectra to be matched within the limits of experimental precision. The values of \( \gamma \), \( \kappa^{-1} \), and \( \tau \) determined at \( T - T_c = 0.05, 0.1, 1, 2, \) and \( 5^0\)K were used to obtain estimates of the constants in the expressions

\[
\kappa = A(T - T_c)^n \quad \text{(3.5a)}
\]

\[
\gamma = B(T - T_c)^m \quad \text{(3.5b)}
\]

It was found that the values of \( n \), \( A \), and \( m \) obtained this way were in reasonable agreement with previous estimates and measurements.

In the preceding paragraphs, the focus has been on the construction of the structure factor \( S(k,\omega) \) defined in Eq. (2.2). Owing to the small dependence of \( \varepsilon \) on temperature, this has been reduced to a problem of constructing the density-density correlation function, in terms of which

\[
S(k,\omega) = 2Re \int_0^\infty dt \ e^{-i\omega t} \langle \Delta \rho(-k,\omega)\Delta \rho(k,\omega) \rangle \quad \text{(3.6)}
\]

where \( \Delta \rho(k,t) \) is the \( k \)-th Fourier mode of the density fluctuations. Both structural and thermal relaxation processes may be studied in considerable detail by analyzing the shifts and widths in the experimentally observed
S function within the framework of such theoretical calculations.

Additional types of relaxation which may occur due to the presence of more than one component may also be studied in a similar fashion from both the experimental and theoretical standpoints. The most important new process to consider is the relaxation of concentration fluctuations by the mechanisms of diffusion and reaction.

Simple model calculations may be done which will illustrate the effects of each of these modes of relaxation. Consider a two-component mixture. If one component, the solvent, is present in great excess over the concentration $c$ of the other, a diffusion equation for the fluctuations in $c$ may be written:

$$
\left[ \frac{\partial}{\partial t} - D \nabla^2 \right] \Delta c(x, t) = 0 ,
$$

(3.7)

where $D$ is the diffusion coefficient. In this model, all fluctuations of $S$, $p$, and mass velocity $u$, are ignored in order to see how the diffusion process affects the scattered light spectrum, thus the dielectric constant fluctuations will be given by

$$
\Delta \varepsilon(k, t) = \left( \frac{\partial \varepsilon}{\partial c} \right)_0 \Delta c(k, t) .
$$

(3.8)

Transforming Eq. (3.7), the fluctuations of the Fourier components satisfy

$$
\left[ \frac{\partial}{\partial t} + Dk^2 \right] \Delta c(k, t) = 0 .
$$

(3.9)
Thus, the spectral structure associated with the diffusion process is

\[
S_D(k, \omega) = \left( \frac{\partial \varepsilon}{\partial c} \right)^2 \frac{V k_B T}{(\partial \mu/\partial c)} \frac{2Dk^2}{(Dk^2)^2 + \omega^2}
\]  

(3.10)

where \( \mu \) is the chemical potential of the solution. As expected, this is a Lorentzian-shaped Rayleigh peak whose half-width is a measure of the diffusion coefficient. Note that in order for this peak to be visible in the spectrum, \( (\partial \varepsilon/\partial c) \) cannot be zero; the dielectric constant of a volume element must change when solute concentration in the element changes. Using a simplified set of hydrodynamic equations, Mountain\(^{19}\) considered both \( T \) and \( c \) fluctuations in an attempt to study critical opalescence in binary mixtures. With appropriate simplifications, he found the result given in Eq. (3.10).

Again considering the model mixture, let there be a reaction between the two components

\[
A \xrightarrow{k_f} \frac{k_f}{k_b} B
\]

(3.11)

If this is a simple unimolecular reaction, then fluctuations \( \Delta \xi = \Delta c_A = -\Delta c_B \) in the concentrations around equilibrium will satisfy a kinetic equation

\[
\frac{\partial}{\partial t} \Delta \xi(x, t) = -\tau^{-1} \Delta \xi(x, t)
\]

(3.12a)

where the chemical relaxation time constant is defined by

\[
\tau^{-1} = k_f + k_b
\]

(3.12b)

and is proportional to the reciprocal of \( \Delta G \) for the reaction. In terms
of the Fourier transform, the relaxation equation is

$$\left[ \frac{\partial}{\partial t} + \tau^{-1} \right] \Delta \xi(k, t) = 0 . \quad (3.13)$$

The temporal behavior of $\Delta \xi(k, t)$ is just a decaying exponential, resulting in a contribution to the structure factor

$$S_R(k, \omega) = \left( \frac{\partial \xi}{\partial \xi} \right)^2 \frac{V k_B T}{(\partial \Delta G / \partial \xi)} \frac{2 \tau^{-1}}{\tau^{-2} + \omega^2} \quad (3.14)$$

where $\Delta G$ is the free energy change for the reaction. This reactive term is discussed in greater length in Chapter Two, but a significant feature to be noted now is that the half-width of this Rayleigh peak is independent of $k$ [cf. Eq. (3.10)]. This is a characteristic difference between processes which depend upon spatial gradients (e.g. diffusion, heat conduction) and those which depend only upon point potentials (chemical reaction).

Although the model calculations just given exemplify the basic results, a calculation which attempts to describe a more realistic model must consider the competition between diffusion and reaction to see more properly how the concentration fluctuations decay. Such calculations have been made a number of times within the restriction that the $T$ and $p$ dependence of $\xi$ was unimportant. $^{20, 21, 22}$ The form of the resulting structure factor is

$$S_{D+R}(k, \omega) = \left[ m_A^2 \alpha_{AA} + m_B^2 \alpha_{BB} + 2m_A m_B \alpha_{AB} \right] \frac{Dk^2}{(Dk^2)^2 + \omega^2}$$

$$+ A(k) \tau \left\{ \frac{\tau^{-1} + Dk^2}{(\tau^{-1} + Dk^2)^2 + \omega^2} - \frac{Dk^2}{(Dk^2)^2 + \omega^2} \right\} \quad (3.15)$$
where \[ m_i = \left( \frac{\partial \epsilon}{\partial \Delta c_i} \right), \quad \alpha_{ij} = \langle \Delta c_i (-k, \omega) \Delta c_j (k, \omega) \rangle \]

and \[
A(k) = m_A^2 \left( k_f \alpha_{AA}^\alpha - k_b \alpha_{AB}^\alpha \right) + m_B^2 \left( k_b \alpha_{BB}^\alpha - k_f \alpha_{AA}^\alpha \right) \\
+ m_A m_B \left( \tau^{-1}_{AB} - k_b \alpha_{BB}^\alpha - k_f \alpha_{AA}^\alpha \right).
\]

When there is no reaction, \( A(k) = 0 \) and the results essentially reduce to those in Eq. (3.10). However, when reactive and diffusive processes both operate to dissipate the concentration fluctuations, there will be a sum of Lorentzians whose half-widths are measures of both modes of decay. Yeh and Keeler\textsuperscript{22} have applied Eq. (3.15) to a study of the association-dissociation in MnSO\textsubscript{4} and ZnSO\textsubscript{4} solutions. This is questionable since charge relaxation has been completely neglected, but may be important in electrolyte solutions. The experiment was performed in such a way that they felt their recorded spectrum \( R(k, \omega) \) could be analyzed according to

\[
R(k, \omega) = B \frac{A(k)}{(\tau^{-1} + b)^2 + \omega^2} \quad (3.16)
\]

where \( b \) is the instrumental linewidth. The chemical reaction relaxation times they obtained this way were in reasonable agreement with the results of corresponding ultrasonic studies.

A more thorough study, including all hydrodynamic effects appropriate to a non-reactive binary mixture, was made by Mountain and Deutch\textsuperscript{23} As expected, there were three peaks in the spectrum. The two Brillouin peaks were again shifted to \( \Omega = \pm c_0 k \) and the half-width \( \Gamma \) contained diffusive terms in addition to the viscosity and thermal conduction.
contributions present in pure fluids. The central peak was a combination of two Lorentzians with amplitudes involving many parameters. Such a complex structure is a direct result of the coupling between diffusion and heat flow. The authors discuss limiting cases of the general expression which may be useful under certain conditions. For example, for very small solute concentrations, the thermal diffusion ratio tends to zero and the Rayleigh peak may be expressed as

\[
S(k, \omega) = \left( \frac{\partial c}{\partial c} \right)^2 \frac{V_k B T}{(\partial \mu / \partial c) (Dk^2 + \omega^2)} + \left( \frac{\partial \epsilon}{\partial T} \right)^2 \frac{V_k B T^2}{C_p (\chi k^2 + \omega^2)}
\]

(3.17)

where \( \chi \) was defined in Eq. (2.10). Since \( \chi \gg D \) for many binary solutions, the central peak will consist of a sharp (i.e. narrow) peak due to diffusion superimposed over a broad thermal peak. In such cases, it may be possible to adequately resolve the experimental Rayleigh peak and determine \( D \) without having to impose macroscopic gradients on the system as is usually the case.

As mentioned before, ionic solutions are probably not well described unless charge relaxation is explicitly considered. Shurr\textsuperscript{24} has made a study of an ionic, reactive system of the form

\[
A^{+z} + B^{-z} \rightarrow C,
\]

(3.18)

where all three species are dilute. The relaxation processes of thermal conduction, viscous drag, chemical reaction, diffusion, and ohmic conduction were all included. Several approximations were introduced to
make the calculations tractable. First, the dependence of the polari-
zability of the system on the concentrations of A, B, and C is assumed
to dominate its T and p dependences. Similarly, the electrochemical
potentials of all the species are assumed to depend only on concentration,
with no T or p dependence. A further approximation was that the
mobilities of the two ionic species, \( u_A \) and \( u_B \), were the same.

There are a couple of novel features of this calculation. Consider
the composition fluctuations around the equilibrium concentrations \( A^0 \),
\( B^0 \), \( C^0 \):

\[
\Delta A(r,t) = A(r,t) - A^0 \\
\Delta B(r,t) = B(r,t) - B^0 \\
\Delta C(r,t) = C(r,t) - C^0
\]

where electroneutrality requires that \( A^0 = B^0 \). It was useful to combine
the concentration fluctuations of A and B to yield two new fluctuating
variables

\[
\Delta_+ = \frac{\Delta A + \Delta B}{2} \quad \text{and} \quad \Delta_- = \frac{\Delta A - \Delta B}{2} .
\]

To see the significance of \( \Delta_- \), consider the local electric charge density
at \( r \),

\[
\rho_c(r,t) = zeA - zeB .
\]

Using Eq. (3.19) in this gives

\[
\rho_c = ze(A^0 + A - B^0 - B) \\
= 2ze\Delta_-
\]
where the electroneutrality condition has been used. In the linearized equations describing the system, the equation for $\Delta_-$ was uncoupled from all other fluctuations. The linearized equations were solved by the usual Fourier-Laplace transform method.

Of special interest was the fairly detailed analysis of fluctuation correlations. In particular, the correlation function from Debye-Hückel theory was used to evaluate initial condition averages of the form $\langle \cdots \rangle$.

The general solution for the structure factor, given in an appendix, was far too complicated to admit of obvious analysis. Results were given for various limits. For very slow reactions, the spectrum is just the diffusion result

$$\frac{I/I_0 \propto c^2 \langle |\Delta c|^2 \rangle}{\omega^2 + \left( \frac{Dc k^2}{c^2} \right)^2} \left( \alpha^2 \frac{Dk^2}{\omega^2 + (Dk^2)^2} + \alpha^2 \frac{Dk^2}{\omega^2 + (Dk^2)^2} \right) \right.$$  

$$= \frac{Dk^2}{\omega^2 + \left( \frac{Dk^2}{\omega^2 + (Dk^2)^2} \right)^2} \left( \alpha^2 \frac{Dk^2}{\omega^2 + \left( \frac{Dk^2}{\omega^2 + (Dk^2)^2} \right)^2} \right)$$

(3.23)

where $\alpha = \frac{\alpha_A + \alpha_B}{2}$. One sees that the charge fluctuations experience additional damping due to conduction.
For fast reactions, the third term in Eq. (3.23) is unchanged, while both of the others show reaction effects. An important fact is that all reactive contributions are multiplied by the factor \((a_+ - a_-)\). This shows that in this model, the spectrum cannot be influenced by the reaction if there is no change of polarizability in the transition from reactants to products. The fast reaction results were given in two limits, low frequency and high frequency, but as is commonly the case with solutions produced by this method, a large amount of algebra remains to be done to get half width and Brillouin shift information.

It remains now to discuss the papers \(^{25,26,27,28}\) which contain the foundation for the present work. There are two aspects of these studies which invite comment. Regarding the specific systems and the thermodynamic and hydrodynamic equations used to describe them, it may be said that these studies represent one of the most thorough investigations of multicomponent fluids which have appeared in the literature. Blum and Salsburg \(^{25}\) first did a detailed spectral analysis for a fluid in which \(n\) chemical reactions occur, neglecting only diffusion, and gave explicit expressions for line widths and displacements for the case of one reaction. Intensities were not considered. Blum \(^{26}\) then did the same analysis for a multicomponent fluid, including diffusion and excluding reaction. He also gave the actual intensity expressions for a binary mixture and for an infinitely dilute solution of rigid polymers. Blum and Salsburg \(^{27}\) next did a complete spectral analysis (through first order) of the multicomponent fluid with both diffusion and chemical reactions included. This work was continued by Blum \(^{28}\) with evaluation of total integrated intensities for the diffusion and reaction modes of relaxation.
Of as much interest, theoretically, as the actual results these authors have obtained, is the technique they developed for doing the calculations. The use of a matrix formulation allows a large part of the analysis to be performed with the powerful tools available in matrix algebra. At best, however, there is only a moderate reduction of effort; the problem is still quite complicated. Specifically, half-widths and displacements are found as the roots of a characteristic equation for the matrix describing the system, and this is precisely the equation which must be solved when the inverse Laplace transform is computed in the ordinary approach.

As is usually the case, a matrix formalism allows a very clean and elegant presentation of the calculation, and the computational details are well-organized, which aids greatly in avoiding algebraic errors. Even this alone would make it worthwhile to pursue such a method.

A conceptual innovation offered by this technique is the "normal mode" analysis of the fluctuations in the system. For every normal mode there is one spectral peak, the intensity of which may be expressed in terms of the eigenvectors for that mode. In Chapter Two, the reader may find additional discussion of the method and obvious illustrations of the remarks already made.
APPENDIX: LORENTZIAN LINE SHAPE CHARACTERISTICS

A Lorentzian shape function is one of the form

\[ L(\delta, \beta; \omega) = \frac{\delta}{\delta^2 + (\beta - \omega)^2} \]  \hspace{1cm} (A1)

where \( \delta \) and \( \beta \) are constants. The spectral structure factors usually can be written as

\[ S(\omega) = L(\delta, \beta; \omega) I_0; \]  \hspace{1cm} (A2)

this is the function which is experimentally observed.

The simplest property of \( S \) is the position of its maximum, \( \omega_{\text{max}} \). Setting \( (dL/d\omega) = 0 \) gives

\[ \omega_{\text{max}} = \beta \]  \hspace{1cm} (A3)

The maximum value of \( L \) is

\[ L(\beta) = \delta^{-1} \]  \hspace{1cm} (A4)

Thus, a measurement of the absolute maximum of the intensity \( S(\beta) \), even in those cases where it is possible, yields only the combination \( I_0/\delta \).

There are two other characteristics of the curve from which \( I_0 \) and \( \delta \) may be separately evaluated. The first of these is the half width at half maximum, \( \Delta \omega \). It is defined as the value of \( |\beta - \omega| \) at the point \( \omega \) where the intensity has fallen to half its maximum value,

\[ \frac{\delta}{\delta^2 + (\Delta \omega)^2} = \frac{1}{2} \delta^{-1}. \]  \hspace{1cm} (A5)
Solving this gives
\[ \Delta \omega = \delta. \tag{A6} \]

Finally, integration of \( L \) over all \( \omega \) just gives \( \pi \). The experimental observable is then
\[ S_{\text{tot}} = \int_{-\infty}^{\infty} S(\omega) d\omega = \pi I_0. \tag{A7} \]

It is, therefore, not difficult to evaluate the parameters in Eq. (42) in terms of the experimental parameters \( \omega_{\text{max}}, \Delta \omega, \) and \( S_{\text{tot}} \).
REFERENCES


9. See reference [2]. Several comments about the method here are to be found in Van Hove's paper, reference [7], as well.

10. In the appendix to this chapter, the characteristics of Lorentzian peak shapes are derived and discussed.


CHAPTER TWO
CHAPTER TWO. LIGHT SCATTERING FROM THE
CHEMICALLY REACTIVE EULERIAN FLUID

This chapter is composed of a manuscript submitted to the Journal of Chemical Physics. The complete title is "Light Scattering from Chemically Reactive Fluids. IV. Intensity Calculations for the Eulerian Fluid with One Reaction." Since its publication, a few minor changes have been made, but they have no effect on the results.

In this chapter, the hydrodynamic equations for the reactive Eulerian fluid (zero transport coefficients, one chemical reaction) have been used in the thermodynamic approach to calculate in detail the spectrum of scattered light. The mathematical technique employed was the matrix eigenvalue formulation previously introduced. The method focuses on a particular matrix which is easily derived from the linearized hydrodynamic equations. The fluctuations of the set of independent variables are resolved into normal modes of relaxation. Each mode contributes one peak to the spectrum; the position and half-width of the peak are furnished directly by the eigenvalue while the intensity is calculated from the corresponding normal mode projection matrix. Some general relationships between positions and half-widths are derived. The Rayleigh peak due primarily to chemical reaction relaxation is considered in detail. Various intensity ratios involving this peak are calculated, and simple criteria are set forth for determining whether it will be intense enough to be experimentally observed. If it is observable, the reaction rate constant can be obtained from measurements of its half-width. Two other chemical relaxation effects, dispersion of the sound speed and
skewing of the Brillouin peaks, are also examined. For small scattering angles and very fast reactions, the rate constant may be extracted from measurements of the sound speed dispersion. The range of relaxation times for which experiments seem feasible is $10^{-4} - 10^{-11}$ sec.
1. INTRODUCTION

In recent years a number of articles have been written on the theory of the spectral distribution of light scattered from a chemically reactive fluid.\textsuperscript{1-7} The theoretical work on this problem has been much more extensive than the experimental work\textsuperscript{8,9} partially because the theoretical papers have offered little guidance for the experimentalists.

Some of the analyses\textsuperscript{1,3,8,9} have been limited in scope and are primarily elementary model calculations which illustrate the major effects of the chemical reaction processes. These calculations tend to ignore hydrodynamic fluctuation effects. The more general papers\textsuperscript{2,4,5,7} are quite formal in nature and present the results in such abstract form that it is almost impossible to apply them.

The complete hydrodynamic fluctuation analysis, which forms the core of these phenomenological theories of light scattering, is rather involved and leads to complicated expressions describing the intensity of the scattered light. One of the challenges which still remains is to carry the analysis to the point where one can make detailed calculations for real chemical systems, and at the same time give a presentation which is comprehensible by both the experimentalist and the theoretician.

This article is intended as a step toward accomplishing these goals. Such a treatment has already been afforded the non-reactive fluid in the excellent article by Mountain and Deutch.\textsuperscript{10} We have chosen to treat the model of a fluid where all dissipative processes except chemical reactions
are neglected. The model is known as the Eulerian model of a compressible fluid. It has the advantage of allowing one to present the results in explicit detail but still in manageable form. The results are directly applicable to systems with very fast chemical reactions, but in a longer range context, the results represent a limiting case of the more general analysis which should incorporate diffusion, viscosity, thermal conductivity and other transport phenomena.

Comments on Perturbation Methods

In addition to the previously noted advantage, the Eulerian model treated in this article also illuminates a basic error of procedure in some of the previous general theories.\textsuperscript{4,5,7} In general, the analyses have been carried out for the limit of long wavelength fluctuations by making formal expansions in powers of the wave number, k. This procedure is adapted from the standard way of treating non-reactive fluids\textsuperscript{10} where it is valid and applicable. In the case of chemical reactions, however, this procedure, while mathematically valid, is only applicable to experiments at very small scattering angles (typically for $\theta < 10^{-3}$ degrees). The Eulerian model not only clearly indicates why chemical processes must be analyzed by a different perturbation technique than other transport phenomena, but also introduces an appropriate method that can be used in the more general case.

Sections II - VII contain the formal analysis of the model. We focus our attention on obtaining the time dependence of the various spatial
Fourier components of the fluctuating hydrodynamic variables. The results are expressed as a linear combination of "hydrodynamic modes", and we emphasize the one-to-one correspondence between these modes and the Lorentzian terms in the light scattering spectrum.

Sections VIII and IX contain the presentation and analysis of the results. Unfortunately, they cannot be read independently of the earlier formal analysis, but hopefully only moderate attention to the details of the previous sections will be required to follow them.

Section X contains the concluding remarks.

2. LIGHT SCATTERING FORMALISM

In the thermodynamic theory of light scattering, the random thermal motion of the molecules results in the production of fluctuations in a complete set of local hydrodynamic variables, which in turn gives rise to fluctuations in the dielectric constant. The choice of the independent variables is somewhat arbitrary, but we have selected the set

\[ \{ S, u, p, \lambda \}, \]  

where \( S \) is the local specific entropy, \( S(r, t) \), \( u = u(r, t) \) is the local barycentric velocity, \( p = p(r, t) \) is the local pressure, and \( \lambda = \lambda(r, t) \) is a set of independent progress variables for the chemical reactions.\textsuperscript{11}

Fluctuations in these variables result in local variations of the dielectric constant \( \varepsilon(r, t) \). Consistent with the usual\textsuperscript{12} assumptions of irreversible thermodynamics, we regard \( \varepsilon \) as a function of the local
thermodynamic variables \((S, p, \lambda)\), in fact the same function one would determine from equilibrium measurements. Thus

\[ \varepsilon = \varepsilon(S, p, \lambda), \quad (2.2) \]

and variations in \(\varepsilon\) are given by

\[ \Delta \varepsilon = (\partial \varepsilon / \partial S)_{p, \lambda} \Delta S + (\partial \varepsilon / \partial p)_{S, \lambda} \Delta p + (\partial \varepsilon / \partial \lambda)_{S, p} \Delta \lambda. \quad (2.3) \]

The intensity of scattered light, \(I(R_o, k, \omega)\), at a position \(R_o\) from the scattering sample is determined from the dielectric constant fluctuations by the expression\(^ {13}\) (see Chapter One)

\[ I(R_o, k, \omega) = I_o \left( k / (k_o)^4 / 32\pi R_o^2 \right) \sin^2 \phi S(k, \omega), \quad (2.4) \]

where \(k = k_o - k\) and \(\omega = \omega_o - \omega_s\). The wave vector and frequency of the incident radiation is denoted by \(k_o\) and \(\omega_o\) respectively, while the corresponding quantities for the scattered radiation are denoted by \(k_s\) and \(\omega_s\). The magnitude of \(k\) is related to the scattering angle \(\theta\) by

\[ k = 2n k_o \sin(\theta/2), \quad (2.5) \]

where \(n\) is the index of refraction of the fluid. \(I_o\) is the intensity of the incident radiation, and \(\phi\) is the angle between the electric vector \(E_o\) of the incident radiation and \(R_o\).

The generalized structure factor, \(S(k, \omega)\), is defined by the following equations

\[ S(k, \omega) = 2 \Re S(k, \omega), \quad (2.6a) \]
\[ S(k, \omega) = \langle \Delta \tilde{\varepsilon}(k, \omega), \Delta \varepsilon(-k, 0) \rangle, \]  
(2.6b)  
\[ \Delta \varepsilon(k, t) = \int dr \Delta \varepsilon(r, t) \exp(ik \cdot r), \]  
(2.6c)  
\[ \Delta \tilde{\varepsilon}(k, \omega) = \int_0^\infty dt \Delta \varepsilon(k, t) \exp(-i\omega t). \]  
(2.6d)

The spatial Fourier transform of \( \varepsilon(r, t) \) is also denoted by the symbol \( \varepsilon \), while \( \tilde{\varepsilon} \) is used to indicate the temporal Fourier transform. The angular brackets \( \langle \ldots \rangle \) indicate an average over all possible fluctuations at \( t = 0 \).

### 3. EULERIAN FLUID MODEL

In our present calculations we restrict ourselves to the model of an Eulerian fluid in which \( n \) independent chemical reactions can take place. The model is characterized by neglecting all transport processes such as diffusion, viscosity, and thermal conductivity. This not only results in considerable mathematical simplification, but also allows the chemical effects to be clearly seen. The model is directly applicable to physical systems in which the chemical relaxation times are much shorter than any of the characteristic relaxation times associated with the transport phenomena.

The equations which describe the system are
\[ \frac{dS}{dt} = -T^{-1} \Delta \varepsilon \cdot \varepsilon, \]  
(3.1a)
\[
\frac{du}{dt} + \nabla \cdot \mathbf{v} = 0 ,
\]

\[(3.1b)\]

\[
\frac{dv}{dt} - \nabla \cdot \mathbf{v} = 0 ,
\]

\[(3.1c)\]

\[
\frac{d\lambda}{dt} = \mathbf{r} ,
\]

\[(3.1d)\]

where

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla
\]

is the barycentric (or convected) derivative. The specific volume is denoted by \( \mathbf{v} \), while \( \lambda = \{ \lambda_1, \lambda_2, \ldots, \lambda_n \} \) and \( \mathbf{r} = \{ r_1, r_2, \ldots, r_n \} \) are the progress variables and rate functions for the \( n \) independent chemical reactions. \( \Delta G = \{ \Delta G_1, \Delta G_2, \ldots, \Delta G_n \} \) are the Gibbs free energy increments for the reactions.

The only phenomenological equation necessary to complete this system of differential equations is

\[
\mathbf{r} = -L \cdot \Delta \mathbf{G} .
\]

\[(3.2)\]

Outline of the Formal Solution

In this section we shall outline the formal mathematical technique we have employed for calculating \( S(k, \omega) \). The detailed results are given later in the paper. For the sake of brevity of presentation, we use a matrix and vector notation.
The hydrodynamic state of the system at position $\mathbf{r}$ and time $t$ is specified by an $n + 3$ component vector $\mathbf{x} = \mathbf{x}(\mathbf{r}, t)$, where

$$\mathbf{x} = \left\{ S, \psi, p, \lambda \right\}. \quad (3.3)$$

We have introduced the new variable

$$\psi \equiv - \nabla \cdot \mathbf{u}.$$  

In our analysis we will assume that $\varepsilon$ is independent of $\psi$, i.e. $\partial \varepsilon / \partial \psi = 0$. We will also assume that fluctuations in $\psi$ are independent of fluctuations in the thermodynamic variables.\textsuperscript{13a}

After taking the divergence of Eq. (3.1b), we may write the set of equations describing the Eulerian fluid in the compact form

$$\partial \mathbf{x} / \partial t = A(\psi) \cdot \mathbf{x} + \mathbf{e}, \quad (3.4)$$

where $A(\psi)$ is an operator matrix whose explicit form is given in Section IV. The vector $\mathbf{e}$ consists of the terms that are not explicitly linear in $\mathbf{x}$.

Equation (3.4) represents a set of non-linear differential equations which we make no attempt to solve. We are not interested in the actual state vector $\mathbf{x}(\mathbf{r}, t)$, but rather in its fluctuations around a uniform equilibrium state vector $\mathbf{x}^0$. Let

$$\mathbf{x} = \mathbf{x}^0 + \hat{\mathbf{x}}, \quad (3.5)$$

where $\hat{\mathbf{x}}$ represents the fluctuations and $\mathbf{x}^0$ satisfies the equation

$$\partial \mathbf{x}^0 / \partial t = A^0(\psi) \cdot \mathbf{x}^0 + \mathbf{e}^0. \quad (3.6)$$
The superscript zero indicates evaluation in the equilibrium state \( x^0 \).

The operator matrix \( \hat{A} \) can also be written in the form

\[
\hat{A} = \hat{A}^0 + \hat{A},
\]

while the vector \( \hat{e} \) may be expanded as

\[
\hat{e} = e^0 + \left( \frac{\partial e}{\partial x} \right)^0 \cdot \hat{x} + \ldots.
\]

Equation (3.4) is next linearized in terms of \( \hat{x} \). The general form of the linearized equation is

\[
\left( \frac{\partial \hat{x}}{\partial t} \right) = \left[ \hat{A}^0 (q) + C^0 \right] \cdot \hat{x},
\]

(3.7)

\[
C^0 = \left( \frac{\partial e}{\partial x} \right)^0.
\]

Since the unperturbed state is uniform with no spatial dependence, we can proceed directly to the calculation of the spatial Fourier components of \( \hat{x} \). Define

\[
a(k, t) = \int \hat{x}(r, t) \exp(ik \cdot r) \, dr,
\]

(3.8)

where the integral is taken over the entire scattering volume. Applying this transform to Eq. (3.7), and noting that the operator \( \nabla \) in \( r \)-space becomes the operator \( -ik \) in \( k \)-space, \( a \) is seen to satisfy the homogeneous equation

\[
\frac{da}{dt} = M \cdot a,
\]

(3.9)

where
\[ M = [A^0(-ik) + C^0] , \]  

(3.10)

and \( \frac{d}{dt} \) is now a total time derivative.

The formal solution to Eq. (3.9) is

\[ a(k, t) = \exp(Mt) \cdot a(k, 0) . \]  

(3.11)

The matrix \( M \) is an \( n + 3 \) rowed square matrix having \( n + 3 \) distinct

eigenvalues \( \mu_0, \mu_+, \mu_-, \mu_1, \ldots, \mu_n \) which we denote by \( \mu_1 \). The \( \mu_1 \) are

the zeros of the characteristic polynomial

\[ \tilde{f}(\mu) = \det(\mu I - M) = \prod_{i=1}^{n} (\mu - \mu_i) . \]  

(3.12)

Having obtained the eigenvalues of \( M \), we may expand the matrix exponential

as follows \(^{14}\):

\[ \exp(Mt) = \sum_j \mu_j^t \tilde{F}_j (M) / \tilde{F}_j (\mu_j) , \]  

(3.13)

where

\[ \tilde{F}_j (\mu) = \tilde{f}(\mu) / (\mu - \mu_j) . \]  

(3.14)

More explicitly,

\[ \tilde{F}_j (M) = \prod_{i \neq j} (M - \mu_i I) , \quad \tilde{F}_j (\mu_j) = \prod_{i \neq j} (\mu_j - \mu_i) . \]  

(3.15)

Substituting from Eq. (3.13) into Eq. (3.11) gives

\[ a(k, t) = \sum_j \mu_j^t \tilde{F}_j \cdot a(k, 0) , \]  

(3.16)
with

\[ M_j \equiv \frac{\tilde{F}_j(M)}{\tilde{F}_j(\mu_j)}. \tag{3.17} \]

In Eq. (3.16) we see that \( a(k,t) \) is written as a sum of \( n + 3 \) terms, each term having a time dependence described by a simple exponential. Each term in this sum is called a "hydrodynamic mode", and we shall refer to the \( n + 3 \) hydrodynamic modes of the Eulerian fluid.

Referring to Eq. (2.3), we can now relate the fluctuation in \( \varepsilon \) to the components of \( a \) given in Eq. (3.16). First of all, including the term \( (\partial \varepsilon / \partial \psi) = 0 \), we can write

\[ \Delta \varepsilon = a(k,t) \cdot (\partial \varepsilon / \partial x)^0, \tag{3.18} \]

and from Eqs. (2.6d), (3.16), and (3.18) we find

\[ \Delta \varepsilon(k, \omega) = (\partial \varepsilon / \partial x)^0 \cdot b(k, \omega), \tag{3.19a} \]

\[ b(k, \omega) = \sum_j L_j(k, \omega) M_j(k) \cdot a(k, 0), \tag{3.19b} \]

\[ L_j(k, \omega) = \begin{cases} - [\mu_j(k) - i\omega]^{-1}, & \text{Re } \mu_j < 0 \\ \pi \delta(\omega), & \mu_j = 0. \end{cases} \tag{3.19c} \]

The structure factor defined in Eq. (2.6a) can now be written as a sum of \( n + 3 \) terms, \( S_j(k, \omega) \), each of which may be called a hydrodynamic mode structure factor.
\[ S(k, \omega) = 2 \sum_j S_j(k, \omega) \quad (3.20a) \]

\[ S_j(k, \omega) = \Re \{ L_j(k, \omega) P_j(k) \} \quad (3.20b) \]

\[ P_j(k) = (\partial \varepsilon / \partial x)^\circ \cdot M_j(k) \cdot G^*(\partial \varepsilon / \partial x)^\circ \quad (3.20c) \]

\[ G = \langle a(k,0) a(-k,0) \rangle \quad (3.20d) \]

With the defining of \( S_j(k, \omega) \) we have established the one-to-one correspondence mentioned earlier; \( S_j(k, \omega) \) is a Lorentzian peak due to relaxation of the \( j \)-th hydrodynamic mode.

The following four sections discuss the detailed form of the matrix \( M \), the evaluation of \( G \) (which involves the statistical averaging), the explicit forms of the \( S_j \) in terms of the eigenvalues of \( M \), and finally, the actual calculation of the eigenvalues.

4. HYDRODYNAMIC ANALYSIS

Following the formal analysis of Section III, we first construct the matrix \( \Lambda(\upsilon) \) and the vector \( e \) shown in Eq. (3.4).

Taking the divergence of Eq. (3.1b) we obtain

\[ -\partial \psi / \partial t + (\upsilon \cdot \nabla)^2 + \nabla \cdot (\nabla \psi) p + \nabla \cdot (u \cdot \nabla u) = 0 \quad , \quad \psi = -\nabla \cdot u \quad . \]

With the vector identity \( \nabla \cdot (u \cdot \nabla u) = -u \cdot \nabla \psi + \nabla u \cdot \nabla u \), this can also be written in the form
\[ \frac{\partial \psi}{\partial t} = -u \cdot \nabla \psi + (\nabla \nabla + \nabla \nabla) p + \nabla u \cdot \nabla u. \]  \hspace{1cm} (4.1)\\

Equation (3.1c) for the specific volume is now replaced by an equation for the pressure through use of the relation

\[ \frac{dp}{dt} = \frac{(\partial v}{\partial p})^{-1}_{S,p} \]

\[ \times \left[ \frac{dv}{dt} - \frac{(\partial v}{\partial S})_{S,p} \cdot dS/dt - \frac{(\partial v}{\partial \lambda})_{S,p} \right. \]

\[ \left. \cdot \frac{d\lambda}{dt} \right] \hspace{1cm} (4.2)\]

Using Eqs. (3.1a), (3.1c), and (3.1d), and the thermodynamic identities in Appendix A, Eq. (4.2) takes the form

\[ \frac{dp}{dt} = \left( \frac{c_o^2}{v} \right)(\psi - \sigma L \cdot \Delta G). \]  \hspace{1cm} (4.3)\\

As our basic set of differential equations we take Eqs. (3.1a), (4.1), (4.3), and (3.1d), in that order. The matrix \( A(\nabla) \) appearing in Eq. (3.4) is then

\[ A(\nabla) = \begin{bmatrix}
-u \cdot \nabla & 0 & 0 & 0 \\
0 & -u \cdot \nabla & \nabla \nabla + \nabla \nabla & 0 \\
0 & c_o^2 / v & -u \cdot \nabla & 0 \\
0 & 0 & 0 & I_n (-u \cdot \nabla)
\end{bmatrix} \]  \hspace{1cm} (4.4)\\

where \( I_n \) denotes the \( n \times n \) unit matrix. The vector \( e \) is

\[ e = \| T^{-1} \Delta G \cdot L \cdot \Delta G, \nabla u : \nabla u, \quad -(c_o^2 / v) \sigma \cdot L \cdot \Delta G, \quad -L \cdot \Delta G \|. \]  \hspace{1cm} (4.5)
Fluctuation Theory

In a simple application of perturbation theory to the solution of Eq. (3.4) we write

\[ \sim x = \sim x^0 + \sim \hat{x}, \quad \sim A = \sim A^0 + \sim \hat{A}, \quad \sim e = \sim e^0 + \sim \hat{e}. \]  

(4.6)

The reference state \( \sim x^0 \) is a uniform, time-independent equilibrium state, thus \( \sim u^0, \sim \psi^0 \), and \( \sim (\Delta G)^0 \) all vanish. This implies \( \sim \hat{A} \cdot \sim x^0 = 0 \), and the linearized form of Eq. (3.4) becomes

\[ \sim (\partial \sim x / \partial t) = \sim [\sim A^0(\sim \psi) + \sim C^0] \cdot \sim \hat{x}, \]

with

\[ \sim A^0(\sim \psi) = \begin{pmatrix} 0 & 0 & \sim v^0 & 0 \\ 0 & 0 & \sim v^0 \sim v^2 & 0 \\ 0 & 0 & \sim c_0^2 / \sim \psi^0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \]

(4.7)

\[ \sim C^0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ d \sim L \cdot \sim G_S & 0 & d \sim L \cdot \sim G_p & d \sim L \cdot \sim \Lambda \\ -\sim L \cdot \sim G_S & 0 & -\sim L \cdot \sim G_p & -\sim L \cdot \sim \Lambda \end{pmatrix}, \]

(4.8)

and
\[ d = - (c_o^2 / \nu^0) \sigma, \quad \Lambda = (\partial \Delta G / \partial \lambda)^0 \] 
\[ G_S = (\partial \Delta G / \partial S) p, \lambda, \quad G_p = (\partial \Delta G / \partial p) S, \lambda. \]

In the development that follows, the superscript zero will be dropped with the understanding that all the thermodynamic properties are equilibrium properties. The components of \( G^0 \) may be put in more convenient form using the identities in Appendix A.

The Matrix \( M \)

The matrix \( M \) defined in Eq. \((3.10)\) may now be obtained from Eqs. \((4.7)\) and \((4.8)\). The result is written in block form as

\[
M = \begin{bmatrix}
0 & \tilde{0} \\
\tilde{M}_{21} & M_{22}
\end{bmatrix}, \quad (4.9)
\]

where \( \tilde{M}_{21} \) is the \( n + 2 \) dimensional column vector

\[
\tilde{M}_{21} = \begin{bmatrix}
0 \\
(c_o^2 / \nu) (T/C_p, o) \sigma L \Delta S \\
(T/C_p, o) L \Delta S
\end{bmatrix}, \quad (4.10)
\]
and $M_{22}$ is the $(n+2) \times (n+2)$ matrix

$$M_{22} = \begin{pmatrix} 0 & -vk^2 & 0 \\ c_0^{-2} & -c_0^{-2} & (c_0^{-2} v) \sigma \Omega \\ 0 & -vL \cdot \sigma & \Omega \end{pmatrix}.$$  \hspace{5mm} (4.11)

We have used the abbreviation

$$\tilde{\Omega} = -L \cdot \Lambda.$$  \hspace{5mm}

Since Eq. (3.7) is rotationally invariant, only the magnitude of $k$ is important here and we shall discontinue its vectorial designation.

The characteristic polynomial $\tilde{f}(\mu)$ is determined by

$$\tilde{f}(\mu) = \det(\mu I - M) = \mu \det(\mu I - M_{22}).$$  \hspace{5mm} (4.12)

One Reaction Case

To obtain explicit results, we now specialize to the case of one independent chemical reaction $(n = 1)$, and introduce the chemical relaxation time, $\tau$, by

$$\tau^{-1} S,p \equiv -\tilde{\Omega} = L \Lambda.$$  \hspace{5mm} (4.13)

In terms of this relaxation time we define two reduced parameters,

$$\zeta \equiv \tau \mu,$$  \hspace{5mm} (4.14)

$$z \equiv \tau c_0 k.$$  \hspace{5mm} (4.15)
\[ B \equiv \tau M, \]  
(4.16)

while \( z \) can be considered a dimensionless wave number. In a similar fashion we define

\[ F_j(B) = \tau^{3/2} F_j(M), \quad F_j(\zeta_j) = \tau^{3/2} F_j(\mu_j). \]  
(4.17)

The characteristic polynomial for the matrix \( B \) is found to be

\[ f(\zeta) = \det(\zeta I - B) = \tau^{4/2} f(\mu) \]

\[ = \zeta(\zeta^3 + \theta \zeta^2 + z^2 \zeta + z^2). \]  
(4.18)

The parameter \( \theta \) which we have introduced is determined by the sound speed dispersion

\[ \theta \equiv \frac{c_o^2}{c_e^2} = \tau^{-1} + c_o^2 \overline{\omega}^2. \]  
(4.19)

Eigenvalue Problem

For reasons which will become obvious as we continue, we denote the four eigenvalues of \( B \) by \( \zeta_0, \zeta_1, \zeta_+, \) and \( \zeta_-; \) these are the four roots of the secular equation

\[ f(\zeta) = 0. \]
The first root which is apparent from Eq. (4.18) is

\[ \tau_0 = 0. \]

The zero value is a result of neglecting diffusion and thermal conductivity. The "hydrodynamic mode" associated with this eigenvalue is intimately related to entropy fluctuations, and referring to Eq. (3.16), we see that this mode is not damped in time for our model.

The second eigenvalue, \( \tau_1 \), is taken as the real root of the cubic equation

\[ F_0 (\tau) = f(\tau)/\tau = 0. \quad (4.20) \]

Perturbation expansions will later be developed for \( \tau_1 \), but in general we can say that \( \tau_1 \) will be negative and correspond, in Eq. (3.16), to a non-propagating "hydrodynamic mode" which is damped in time. In the spectral analysis this term will give rise to a Lorentzian peak centered at \( \omega = 0 \).

The remaining two eigenvalues, \( \tau_{\pm} \), are the two zeros of the quadratic equation

\[ 0 = F_0 (\tau)/ (\tau - \tau_1) \]

\[ = \tau^2 + (\theta + \tau_1)\tau - \zeta^2/\tau_1. \quad (4.21) \]

More explicitly,

\[ \tau_{\pm} = \frac{\theta}{2} [ - \theta - \tau_1 \pm \sqrt{h(\tau_1)} ], \quad (4.22) \]

\[ h(\tau_1) = \tau_1^{-1} [ \tau_1^3 + 2\theta \tau_1^2 + \vartheta^2 \tau_1 + 4\zeta^2 ]. \]
The eigenvalues determined formally by Eq. (4.22) will be complex conjugates of one another (\( h < 0 \)), and represent the propagating sound modes of relaxation. These will produce the two Brillouin peaks centered around \( \tau \omega = \pm \frac{1}{2} \sqrt{|h|} \).

The Hydrodynamic Modes

In order to make the decomposition into hydrodynamic modes shown in Eq. (3.16) we need the functions \( F_0(\zeta) \), \( F_1(\zeta) \), and \( F_\pm(\zeta) \). From Eqs. (4.20) and (4.18), we have

\[
F_0(\zeta) = \zeta^3 + \theta \zeta^2 + z^2 \zeta + z^2, \tag{4.23}
\]

while the remaining three functions have the form

\[
F_j(\zeta) = f(\zeta)/(\zeta - \zeta_j)
= \zeta^3 + (\theta + \zeta_j)\zeta^2 + (\zeta_j^2 + \theta \zeta_j + z^2)\zeta \quad j = 1, \pm. \tag{4.24}
\]

Since \( \zeta_0 = 0 \), we have

\[
F_0(\zeta_0) = z^2, \tag{4.25}
\]

and

\[
F_j(\zeta_j) = \zeta_j(3\zeta_j^2 + 2\theta \zeta_j + z^2), \quad j = 1, \pm. \tag{4.26}
\]

The matrix functions \( F_0(\mathbf{B}) \), \( F_1(\mathbf{B}) \), and \( F_\pm(\mathbf{B}) \) may be written in the following form after some manipulations outlined in Appendix D.
\[ F_0(B) = z^2 \]
\[ F_j(B) = \begin{pmatrix} 0 & 0 \\ V_j & F_j(B) \end{pmatrix}, \quad j = 1, \pm \]
\[ V_j = \begin{pmatrix} 0 \\ T\Delta S/\Lambda C_{P,0} \end{pmatrix} \]

and
\[ F_j(B) = \begin{pmatrix} -\zeta_j z^2 \sigma/\tau \\ -\zeta_j \zeta_j^2 c_o^2 \sigma/v \\ -\zeta_j^2 + z^2 \end{pmatrix} \]
\[ F_j(B) = \begin{pmatrix} -z^2(1+\zeta_j) & -\tau v k^2 \zeta_j^2(1+\zeta_j) & \zeta_j z^2 \sigma/\tau \\ \zeta_j^2 c_o^2 \sigma/v & \zeta_j^2(1+\zeta_j) & -\zeta_j^2 c_o^2 \sigma/v \\ -\zeta_j^2 c_o^2 L_o & -\tau v L_o \zeta_j^2 & -z^2 - \zeta_j^2 \end{pmatrix} \]
This completes the analysis of the time dependence of the spatial Fourier transform of the fluctuations $\hat{x}(r,t)$. We next consider the thermodynamic analysis of the initial fluctuations.

5. THERMAL FLUCTUATIONS

In Section IV, the time dependence of the decay of thermal fluctuations in a fluid was calculated from a hydrodynamic theory. The initial fluctuations, whose Fourier components were represented by $a(k,0)$, are assumed to arise from the thermal motion of the molecules. Their explicit effect on the light scattering spectrum is described by the matrix $G$ in Eq. (3.20d). Using the definition given in Eq. (3.8), we can write

$$G = \langle a(k,0) a(-k,0) \rangle$$

$$= \int \int \langle \hat{x}(r_1,0) \hat{x}(r_2,0) \rangle \exp[ik \cdot (r_1 - r_2)] \, dr_1 \, dr_2 . \quad (5.1)$$

Introducing the relative coordinate $R = r_2 - r_1$, we define a correlation matrix $\nu(R)$ by

$$\langle \hat{x}(r_1) \hat{x}(r_2) \rangle = \langle \hat{x}(r_1) \hat{x}(r_1 + R) \rangle$$

$$= \langle \hat{x}(r_1) \hat{x}(r_1) \rangle \cdot \nu(R) , \quad (5.2)$$

with the assumption that $\nu$ depends only on $R$. \

Substituting this last expression into Eq. (5.1), and converting the integral over \( \mathbf{r}_2 \) to one over \( \mathbf{R} \) gives

\[
G = \left[ \frac{1}{V} \langle \hat{x}^{(Q)}(\mathbf{r}_1) \hat{x}(\mathbf{r}_1) \rangle \right] \cdot \mathcal{U}(k),
\]

(5.3)

\[
\mathcal{U}(k) = \int \mathcal{V}(\mathbf{R}) \exp(-i\mathbf{k} \cdot \mathbf{R}) \, d\mathbf{R}.
\]

In a homogeneous isotropic fluid, we expect that \( \mathcal{V}(\mathbf{R}) \) will depend only on \( \mathbf{R} = |\mathbf{R}| \), and that \( \langle \hat{x}^{(Q)}(\mathbf{r}_1) \hat{x}(\mathbf{r}_1) \rangle \) will be essentially independent of the position \( \mathbf{r}_1 \). Letting \( V \) denote the volume of the scattering region, then, we may write

\[
G = V \langle \hat{x} \hat{x} \rangle \cdot \mathcal{U}(k).
\]

(5.4)

There are several standard techniques for evaluating the ensemble average of the dyadic \( \langle \hat{x} \hat{x} \rangle \), but the evaluation of \( \mathcal{U} \) poses a special problem, since \( \mathcal{V}(\mathbf{R}) \) is not known in general. The elements of \( \mathcal{V} \) describe such things as entropy-entropy correlations and pressure-progress variable cross-correlations between neighboring volume elements in the fluid. In our phenomenological theory we deal with macroscopic subsystems, large enough that their parameters can be identified with thermodynamic variables of state, yet small enough that the linear dimensions of the subsystem are much less than the wavelength, \( 2\pi/k \), of light. Thus, the problem of discussing the correlations between the fluctuations in neighboring subsystems is actually quite different than treating the correlations between particles at the molecular level. Nevertheless, we shall model our \( \mathcal{V}(\mathbf{R}) \) after the coarse-grained density-density correlation function obtained from molecular theory. \(^{15}\)
A more detailed discussion of $\Upsilon(k)$ is given in Appendix B, but the basic argument is that the components of $\Upsilon(R)$ vanish for $R > R_c$, with $R_c \ll \lambda$. Moreover, we are concerned with the Fourier components of the fluctuations whose wave vectors satisfy $|k| = k \ll 1/\lambda$. Thus,

$$|k \cdot R| \ll 1,$$

and the exponential in Eq. (5.3) can be set equal to unity with the result

$$\Upsilon(k) = 3V_c \Upsilon_0,$$  \hspace{1cm} (5.5)

$$V_c = 4\pi R_c^{3/3},$$

where $\Upsilon_0$ is independent of $k$, and $V_c$ is the "volume of correlation."

The reader will note that we have kept the $k$-dependence in the $L_j$ and $M_j$ factors in Eq. (3.20), but have now neglected it in $\Upsilon$. It is not clear that this inconsistent procedure is valid, but the model calculation in Appendix B is given as a rationalization for this approximation.

Lacking any detailed information about $\Upsilon(R)$, we can go no further in the formal evaluation of $\Upsilon$. To obtain explicit results we simply assume
that $\nu$ is a constant matrix

$$\nu(R) = \nu(R) \mathbf{I},$$  \hspace{1cm} (5.6)

and that the spatial correlation between all local properties is described by the same function $\nu(R)$. Equation (5.6) implies that $U^{\circ}_{0}$ is just the unit matrix, and $G$ finally gets the form

$$G = 3 \nu V_{c} \langle \hat{\mathbf{x}} \hat{\mathbf{x}} \rangle. \hspace{1cm} (5.7)$$

The matrix $\langle \hat{\mathbf{x}} \hat{\mathbf{x}} \rangle$ is calculated using the thermodynamic theory of fluctuations. The theory postulates a Gaussian distribution for the probability of observing the fluctuation $\hat{\mathbf{x}} = \mathbf{x} - \mathbf{x}^{0}$ in volume element $V_{c}$. Denoting this probability by $w(\hat{\mathbf{x}})$, the defining relation is

$$w(\hat{\mathbf{x}}) = A \exp \left[ -\frac{V_{c}/\nu}{2k_{B}} \hat{\mathbf{x}} \cdot \hat{\mathbf{x}} \right], \hspace{1cm} (5.8)$$

where $V_{c}/\nu$ is the number of grams in $V_{c}$ and Boltzmann's constant is $k_{B}$. $E$ is a symmetric positive definite matrix which is derived in Appendix C,

$$E = \begin{pmatrix}
C_{p,o}^{-1} & 0 & 0 & -\Delta S/C_{p,o} \\
0 & X/T & 0 & 0 \\
0 & 0 & v^{2}/c_{o}^{2}T & 0 \\
-\Delta S/C_{p,o} & 0 & 0 & \Lambda/T
\end{pmatrix}. \hspace{1cm} (5.9)$$
\( X \) is the coefficient describing the fluctuations in the hydrodynamic variable \( \psi \), and for our purposes can be left arbitrary. The calculation in Appendix C using the Gaussian probability density gives

\[
\langle \hat{\psi} \hat{\psi} \rangle = (v k_B / V) E^{-1}.
\]

Thus, \( G \) has the explicit form

\[
G = \frac{3v^2 k_B T}{Q}
\]

\[
\begin{pmatrix}
C_{p,0}^2 T & 0 & 0 & C_{p,0} \Delta S \\
0 & Q / k & 0 & 0 \\
0 & 0 & Q c_0^2 / \nu^2 & 0 \\
C_{p,0} \Delta S & 0 & 0 & C_{p,0}
\end{pmatrix}
\]

(5.10)

where

\[
Q = C_{p,0} L - T(\Delta S)^2.
\]

(5.11)

We note that the "volume of correlation," \( V_c \), does not appear in the final result.
6. STRUCTURE FACTOR

From the hydrodynamic and thermodynamic analyses of the preceding sections we have obtained all the factors necessary for the calculation of $S_j(k,\omega)$. Using subscripts to denote partial differentiation, we write

$$\frac{\partial \varepsilon}{\partial x}^0 = \begin{array}{c}\varepsilon_S, 0, \varepsilon_p, \varepsilon_\lambda \end{array}.$$  \hspace{1cm} (6.1)

Because the expressions involving the zero eigenvalue do not have the same general forms as those for the other eigenvalues, the two cases will be treated separately.

Using the definition of $P_j$ given in Eq. (3.20c) and the relation $\mu_o = P_o(B)/P_o(\tau_o)$ gives

$$P_o = A_o [\varepsilon_S C_p, o \Lambda + \varepsilon_\lambda T\Delta S]^2,$$  \hspace{1cm} (6.2)

$$A_o = \frac{3Vv_k_B}{\Lambda Q}$$

For the non-zero eigenvalues, we find the following expression giving $P_j$ as a function of the eigenvalue $\zeta_j(k)$;

$$P_j(k) = A \frac{\varepsilon_p^2(1 + \zeta_j)\zeta_j^2 - 2 \varepsilon_p \varepsilon_\lambda \zeta_j^2 v^2 / \Lambda - \varepsilon_\lambda^2 (v^2 / c_o^2)(\varepsilon^2 + \zeta_j^2) / \Lambda}{\zeta_j(3\zeta_j^2 + 2\theta\zeta_j + z^2)}.$$  \hspace{1cm} (6.3)

$$A = (c_o / v)^2(3 Vv_k_B T)$$
It is possible to considerably simplify Eq. (6.3) by multiplying both
umerator and denominator by the numerator and denominator by the
quantity \( (1 + \zeta_j)/(\zeta_j^2) \). Using the characteristic equation in the form of
the identity

\[
(1 + \zeta_j)(z^2 + \zeta_j^2) = -(\theta - 1)\zeta_j^2,
\]
the expression for \( P_j \) becomes

\[
P_j = A[\epsilon \rho (1 + \zeta_j) - \alpha \epsilon_{\lambda}]^2 / D_j, \quad j=1, \pm
\]

\[
D_j = 2 \zeta_j^2 + (3 + \delta)\zeta_j + 2\theta,
\]

where we have defined the thermodynamic parameter

\[
\alpha = \nu \sigma / \Lambda.
\]

Since the eigenvalues \( \zeta_j \) will be complex in general, we express them
in the form

\[
\zeta_j = -\delta_j + i\beta_j.
\]

We note that \( \delta_j \) is positive semi-definite. Using Eqs. (4.14) and (6.6)
in Eq. (3.19c), we may write the Lorentzian shape factor as

\[
L_j = \begin{cases} 
\tau[\delta_j^2 + (\beta_j - \tau\omega)^2]^{-1} \{\delta_j + i(\beta_j - \tau\omega)\}, & \delta_j > 0 \\
\tau \pi \delta(\beta_j - \tau\omega), & \delta_j = 0.
\end{cases}
\]
Consider now the non-zero eigenvalues. We may separate $P_j$ into its real and imaginary parts by writing

$$P_j = R_j + i I_j,$$  \hspace{1cm} (6.8)

with the result that $S_j$ takes the form

$$S_j = [\delta_j^2 + (\beta_j - \tau \omega)^2]^{-1} \tau R_j \delta_j \delta_j - (\beta_j - \tau \omega) \xi_j,$$  \hspace{1cm} (6.9)

$$\xi_j = I_j / R_j, \quad j = 1, \pm .$$

The factor $\xi_j$ is a measure of the "skewness" of the peak from the symmetric Lorentzian shape. Its contribution is usually so small that it is neglected. When this is the case, the peak associated with $S_j$ can be described by the following measurable quantities:

a) frequency of maximum intensity, \hspace{1cm} $\omega_j = \tau^{-1} \beta_j$ \hspace{1cm} (6.10a)

b) maximum intensity, \hspace{1cm} $S_j^{\text{max}} \equiv S_j(\omega_j) = R_j / (\tau^{-1} \delta_j)$ \hspace{1cm} (6.10b)

c) half-width at half-maximum, \hspace{1cm} $\Delta \omega_j = \tau^{-1} \delta_j$ \hspace{1cm} (6.10c)

d) integrated intensity, \hspace{1cm} $\int_{-\infty}^{\infty} S_j(k, \omega) d\omega = \tau R_j$ \hspace{1cm} (6.10d)

Property d) also holds for the thermal peak, $S_0$. We call $R_j$ the cross section for scattering from the $j$-th hydrodynamic mode. These properties, except d), are slightly modified when the skewing factor $\xi_j$ is included. We shall return to the discussion of this in connection with our analysis of the Brillouin lines.
7. PERTURBATION SOLUTIONS

Up to this point we have directly or indirectly expressed all our results in terms of the real zero, $\zeta_1$, of the function $F_0(\zeta)$ defined in Eq. (4.23). Although the exact form of $\zeta_1$ can be given, it is not a very illuminating result, and moreover cannot be extended to the multi-reaction case. Fortunately there are convenient expansions for the $\zeta_j$ which we now consider.

Long Wavelength Limit

Hydrodynamic analyses are generally valid for long wavelength components of the fluctuations. This type of treatment, which is most appropriate for non-reactive transport phenomena, considers the formal limit as $k \to 0$. An appropriate reduced variable in which to express this limit is $z = \tau_0 k$. Consider the real root of the cubic equation,

$$\zeta^3 + \delta \zeta^2 + z^2 \zeta + z^2 = 0 ,$$

(7.1)

in the form

$$\zeta(z) = \zeta^{(0)} + \zeta^{(1)} z + \zeta^{(2)} z^2 + \cdots .$$

(7.2)

Substituting expression (7.2) into Eq. (7.1) and equating powers of $z$ gives a set of algebraic equations for the $\zeta^{(n)}$. These may be solved to give

$$\zeta_1(z) = -\delta + z^2 \frac{(\theta - 1)}{\theta^2} + z^4 \frac{(\theta - 1)(\theta - 2)}{\theta^4} + \cdots .$$

(7.3)
While Eq. (4.22) may be used to calculate $\zeta_\pm$ from $\zeta_1$, it is just as convenient to use the same method for all three roots. The result is

$$
\zeta_\pm(z) = -\frac{1}{2} z^2(\theta - 1)/\theta^2 - \frac{1}{3} z^4(\theta - 1)(\theta - 2)/\theta^4 + \ldots
$$

$$
\pm i \theta^{-\frac{2}{3}}[z - (1/8)z^3(\theta - 1)(\theta - 5)/\theta^3 + \ldots] .
$$

(7.4)

Chemical Perturbation Expansion

For a wide range of chemical systems $\theta - 1$ is a small parameter, and as such can be used as an expansion parameter to obtain good approximations to the $\zeta_j$. Proceeding as before, we let

$$
\zeta(t) = \zeta^{(0)} + \zeta^{(1)} t + \zeta^{(2)} t^2 + \ldots ,
$$

(7.5)

$$
t = \theta - 1 ,
$$

and substitute into Eq. (7.1). Equating powers of $t$ we get

$$
\zeta_1(t) = -1 - t/s - 2t^2z^2/s^3 + \ldots ,
$$

(7.6)

$$
\zeta_\pm(t) = -\frac{1}{2} t z^2/s + t^2 z^2/s^3 + \ldots
$$

$$
\pm i z[1 - \frac{3}{8} t/s + (1/8)t^2(3 - 6z^2 - z^4)/s^3 + \ldots] ,
$$

(7.7)

with

$$
s = 1 + z^2 .
$$
In a formal sense, this perturbation expansion in powers of $t$ is valid for a much wider range of experimental conditions than the expansion in powers of $k$. Moreover, it corresponds to the usual way of treating chemical reactions in ultrasonic experiments. One must keep in mind, however, the fact that molecular theories indicate that the complete hydrodynamic analysis itself is only valid through terms of order $k^2$. Thus the leading terms in the $t$-expansion which include contributions from all orders of $k$ may be somewhat questionable from a molecular point of view.

**Large $z$ Limit**

There is one other expansion we wish to consider, since it will be of interest to know how the roots of Eq. (7.1) behave for very large $z$. We therefore attempt to find the real root of Eq. (7.1) in the form

$$\zeta_1(1/z) = \zeta^{(0)} + \zeta^{(1)}/z + \zeta^{(2)}/z^2 + \ldots \quad (7.8)$$

Equation (4.22) may then be used to calculate $\zeta_\pm$. The results are

$$\zeta_1(1/z) = -1 - \frac{t}{z^2} + \ldots \quad (7.9)$$

$$\zeta_\pm(1/z) = -\frac{t}{2z^2} + \frac{t^2}{z^2} + \ldots$$

$$\pm iz[1 - \frac{1}{2}t/z^2 - (1/8)t^2/z^2 + \ldots] \quad (7.10)$$
If one carefully expands Eqs. (7.6) and (7.7) in powers of $1/z^2$, assuming $z^2 \gg 1$, it will be found that Eqs. (7.9) and (7.10) result. Thus, the large $z$ behavior of the $\zeta_j$ is contained in the $(\theta - 1)$- expansion and does not need a separate treatment. It is not possible, however, to get Eqs. (7.3) and (7.4) by taking $z^2 \ll 1$ and expanding the $(\theta - 1)$ series in powers of $z$. This is due to the fact that all terms in the $(\theta - 1)$ series contribute to the coefficients of each power of $z$. We conclude that both the $z$- and $t$-expansions are needed to describe the $\zeta_j$ in the whole $z$ domain. Note that large $z$ needs not imply large $k$.

A physical interpretation of the large $z$ limit follows if we regard $(c_0 k)^{-1}$ as a "characteristic time" for hydrodynamic relaxation. Large $z$ then implies the relation $\tau \gg (c_0 k)^{-1}$, which indicates that the characteristic time for reaction is very long. In particular, the $z \to \infty$ limit can be thought of as a sort of "non-reactive" limit. The notion of a time scale defined in this manner by the relaxation time $\tau$ was implicit in the definition of $\zeta$, Eq. (4.16).

8. LORENTZIAN CONTRIBUTIONS TO THE INTENSITY

This section is divided into five major paragraphs. The first three constitute a presentation of the half-widths and cross sections of the central thermal peak $S_0$, the chemical reaction peak $S_1$, and Brillouin peaks $S_\pm$. For all the peaks, the analytical expressions for the cross sections are collected in Appendix E, and only selected expressions will be quoted in this section. The $z$-expansions, valid in the $z \to 0$ limit, are denoted by
a superscript zero, while the \( z \to \infty \) limits of the \( t \)-expansions are denoted by a superscript infinity.

The fourth paragraph discusses the displacement of the Brillouin peaks and the sound speed dispersion relation. The skewing of the Brillouin peaks is examined in the last paragraph.

For economy of expression, we shall continue to employ the following abbreviations:

\[
t \equiv \theta - 1, \quad \alpha = v\sigma/\Lambda, \quad z \equiv \tau c_o k, \quad s \equiv 1 + z^2.
\]  

(8.1)

We also define a new parameter, \( K \), which is a "characteristic wave number" for the system, by

\[
K \equiv (\tau c_o)^{-1}.
\]  

(8.2)

In order to have some numerical values for these and other quantities appearing in the theory, we have prepared Table I from available data\(^{18,19,20}\) on the reaction

\[
\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2
\]

which occurs in liquid \( \text{N}_2\text{O}_4 \). For the calculation of \( z \) we have arbitrarily chosen \( k = 10^5 \text{ cm}^{-1} \).

In general, the value of \( z \) for a particular experimental situation will not be known, but using the estimate \( c_o k \approx 10^{10} \text{ sec}^{-1} \), we may say that most experiments will be carried out in the \( z \to \infty \) limit (assuming relaxation times of \( 10^{-3} \) to \( 10^{-8} \) sec for the reaction). The problem of determining \( z \) for a given system will be discussed in the second paragraph of Section IX.
TABLE I.

Thermodynamic data and calculated parameters for the liquid $N_2O_4 - NO_2$ system at 273°K. Data are taken from Ref. 18-20. The value of $z$ was calculated using a wave number of $10^5$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$</td>
<td>0.692 cm$^3$/gm</td>
</tr>
<tr>
<td>$\beta_o/v$</td>
<td>$1.63 \times 10^{-3}$/deg</td>
</tr>
<tr>
<td>$c_o$</td>
<td>$9.923 \times 10^4$ cm/sec</td>
</tr>
<tr>
<td>$C_{p,o}$</td>
<td>0.367 cal/deg-gm</td>
</tr>
<tr>
<td>$\Delta v/v$</td>
<td>0.4</td>
</tr>
<tr>
<td>$\tau_{S,p}$</td>
<td>$8.67 \times 10^{-4}$ sec</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>193.6 cal/gm</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>0.48 cal/deg-gm</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>57.6 cal/gm</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**THEORETICAL**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>-0.46</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>$2.37 \times 10^{12}$ erg/gm</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$-1.343 \times 10^{-13}$ cm sec$^2$/gm</td>
</tr>
<tr>
<td>$t$</td>
<td>$8.792 \times 10^{-4}$</td>
</tr>
<tr>
<td>$K$</td>
<td>$1.174 \times 10^{-2}$/cm</td>
</tr>
<tr>
<td>$z$</td>
<td>$86.03 \times 10^5$</td>
</tr>
</tbody>
</table>
The "Thermal" Rayleigh Peak

The spectral line due to entropy fluctuations is described by the structure factor

\[ S_{\omega}(\omega) = 2\pi A_{\omega} \delta(\omega) [\varepsilon_s C_{p,s} A + \varepsilon_{\lambda} T\Delta S]^2 , \]  

(8.3)

where the constant $A_{\omega}$ has been defined in Eq. (6.2). Mathematically, the delta function at $\omega = 0$ results from the zero eigenvalue of the matrix $M$, which is associated with the entropy fluctuations. The linearized form of the entropy equation is $\dot{S}/dt = 0$. The physical implication is that in the Eulerian model, entropy fluctuations do not decay in time, and it is this infinite lifetime which gives rise to the zero line width. Nevertheless, it should be noted that this thermal line does contribute correctly to the total scattering cross section (see Section IX).

Inclusion of any of the hydrodynamic relaxation processes into the model will broaden the delta function peak into a Lorentzian form. In this extension of the theory, the zero eigenvalue is replaced by one of the form

\[ \varepsilon_{\omega} = -a k^2 + b k^4 + \cdots , \]  

(8.4)

where $a$ and $b$ are functions of the non-zero transport coefficients. Specifically, for a non-zero thermal conductivity, $\kappa$, we have $a = \tau\nu k/C_{p,e}$ and this line will have a width

\[ \Delta_{\omega}\omega = (\nu k/C_{p,e}) k^2 + \cdots . \]  

(8.5)
The chemical reaction line, to be discussed next, is also a Lorentzian peak centered at \( \omega = 0 \). The observed central peak will therefore be the sum of these two Lorentzians and the finite value of \( \Delta \omega_0 \) may become important in the experimental analysis.

The "Chemical Reaction" Peak

There is a second Rayleigh peak, due primarily to fluctuations of the progress variable, which is described by the structure factor

\[
S_1(k, \omega) = \left[ \delta_1^2 + (\tau \omega)^2 \right]^{-1} \tau R_1 \delta_1.
\]  

(8.6)

The theoretical characterization of \( S_1 \) is one of the major aspects of this article.

The half-width of this peak has the following expansions:

\[
\Delta \omega_1 = \tau^{-1} \left[ 1 + t/s + 2t^2 z^2/s^3 + \cdots \right],
\]  

(8.7)

\[
\Delta \omega_1^{(o)} = \tau^{-1} \left[ t - z^2 t/\theta^2 + \cdots \right].
\]  

(8.8)

In order to examine the \( z \)-dependence of \( \Delta \omega_1 \), and to compare Eqs. (8.7) and (8.8), we utilize the auxiliary function

\[
h(z) \equiv t^{-1} (\tau \Delta \omega_1 - 1).
\]  

(8.9)

In Fig. 1 we have graphed this function as determined from both the \( t \)- and \( z \)-expansions. Note that \( \Delta \omega_1 \) and \( \Delta \omega_1^{(o)} \) are equal through terms of order \( t \) at \( z = 0 \).
Since Eq. (8.8) derives from a series solution of Eq. (7.1) in powers of \( z \), it is clear that it must diverge from the true \( \Delta \omega_1 \) for \( z > 1 \). In fact, Fig. 1 shows significant divergence even for smaller values of \( z \). Now, it is true that the inclusion of more terms in Eq. (8.8) would result in a better approximation to \( \Delta \omega_1 \) in the domain \( z < 1 \). However, higher order terms become increasingly difficult to generate, especially for more complicated models. Thus, we are led to inquire: keeping only terms through \( z^2 \) in Eq. (8.8), to what domain must we restrict \( z \) such that the fractional difference between \( \Delta \omega_1^{(o)} \) and \( \Delta \omega_1 \) is less than some prescribed value, \( a \)? That is, we wish to find the value \( z_o \) for which

\[
\frac{\Delta \omega_1(z_o) - \Delta \omega_1^{(o)}(z_o)}{\Delta \omega_1(z_o)} = a. \quad (8.10)
\]

Neglect of terms of order \( t^2 \) in Eq. (8.7) leads to the formula

\[
z_o^2 \approx \frac{3}{2}[m + (m^2 + 4m)^{\frac{1}{2}}], \quad (8.11)
\]

\[
m = a/t. \quad (8.11)
\]

Assuming a precision of one part in \( 10^5 \) for the experimental data, we have \( a = 10^{-5} \), and for \( t = 10^{-3} \),

\[
z_o \approx 0.32. \quad (8.12)
\]

This value bounds the domain of practical validity of the \( z \)-expansion.
For large $z$ we may take the $z \to \infty$ limit of Eq. (8.7) to get

$$\Delta \omega_1^{(\infty)} = \tau^{-1} [1 + t/z^2 + \ldots] . \quad (8.13)$$

Using this expression in Eq. (8.9) gives the third curve in Fig. 1. We see that $z$ need not be very large for $\Delta \omega_1^{(\infty)}$ to be a very good approximation to $\Delta \omega_1$. If we regard Eq. (8.13) in the same spirit as we did Eq. (8.8), we may ask for the value $z_\infty$ for which

$$\frac{\Delta \omega_1^{(\infty)}(z_\infty) - \Delta \omega_1(z_\infty)}{\Delta \omega_1(z_\infty)} = a \quad . \quad (8.14)$$

Choosing the same values of $a$ and $t$ as before, we get

$$z_\infty \approx 3.2 \quad . \quad (8.15)$$

We have indicated both $\ln z_o$ and $\ln z_\infty$ by vertical lines in Fig. 1.

Note that in the $z \to \infty$ limit, the half-width is

$$\Delta \omega_1^{(\infty)} \sim \tau_{S,P}^{-1} \quad , \quad (8.16)$$

whereas in the $z \to 0$ limit

$$\Delta \omega_1^{(\infty)} \sim \theta \tau_{S,P}^{-1} = \tau_{S,V}^{-1} \quad . \quad (8.17)$$

Comparing Eq. (8.17) with Eq. (8.5) shows that in the limit of zero scattering angle, the half-width of the observed Rayleigh peak is just equal to the rate constant for the reaction, measured at constant entropy and specific volume.
We now consider the cross section $R_1$. It is apparent from Eqs. (6.4), (6.6), (6.8), and (6.10a) that $R_1$ can be expressed as a function of the half-width

$$R_1 = A \frac{[\alpha \varepsilon_\lambda + (\tau \Delta \omega_1 - 1) \varepsilon_p]^2}{2\tau^2 \Delta \omega_1^2 - (3 + \theta) \tau \Delta \omega_1 + 2\theta}.$$  

(8.18)

The $t$- and $z$-expansions of $R_1$ are found in Eqs. (E.2) and (E.3). Since $\tau \Delta \omega_1 - 1 = t \, h(z)$, we see that for all values of $z$, the dominant term in the cross section is $\alpha \varepsilon_\lambda$ with a small $z$-dependent correction from $\varepsilon_p^*$. We may consider $R_1$ to be proportional to the square of an "effective" reaction dependence of $\varepsilon$, denoted by $\varepsilon_\lambda^*$, which is given by

$$\varepsilon_\lambda^* = \varepsilon_\lambda [1 + t \, h(z) \, \varepsilon_p / \alpha \varepsilon_\lambda].$$  

(8.19)

The cross section then takes the compact form

$$R_1 = (\Delta / \Delta_1)(\alpha \varepsilon_\lambda^*)^2,$$  

(8.20)

where $\Delta_1$ is defined in Eq. (E.2). The $z$-dependence of $R_1$ is shown in Fig. 2 for $t = 10^{-2}$ and two possible values of the ratio $b = \alpha \varepsilon_\lambda / \varepsilon_p$.

The $t$-expansion of $h(z)$ has been used.

Using Eq. (E.4) we see that

$$\lim_{z \to 0} \varepsilon_\lambda^* = \varepsilon_\lambda = (\partial \varepsilon / \partial \lambda)_{T,\rho} ,$$  

(8.21a)

and

$$\lim_{z \to \infty} \varepsilon_\lambda^* = \varepsilon_\lambda = (\partial \varepsilon / \partial \lambda)_{S,p} .$$  

(8.21b)
Thus, the asymptotic values of the cross section are

\[ R_1^{(0)} \sim \left( \frac{A}{t \theta} \right) (\alpha \varepsilon_\lambda) \]

\[ R_1^{(\infty)} \sim \left( \frac{A}{t} \right) (\alpha \varepsilon_\lambda)^2 \]  

(8.22a)  

(8.22b)

The Brillouin Peaks

A little reflection on Eq. (6.9) will show that the Brillouin peaks are mirror images of each other; i.e., \( S_-(k_z-\omega) = S_+(k_z+\omega) \). Hence, we discuss only one of the peaks which we arbitrarily choose to be \( S_+ \) and which we denote by \( S_B \). With a similar renaming of the other quantities, the structure factor may be written

\[ S_B = [\delta_B^2 + (\beta - \tau \omega)^2]^{-1} \tau R_B \{ \delta_B - (\beta - \tau \omega) \xi \} . \]  

(8.23)

Temporarily neglecting \( \xi \), the half-width of this peak is described by

\[ \Delta \omega_B = \left( \frac{t}{2\tau} \right) [z^2 + 2tz^2 - 2z^3 + \ldots] , \]  

(8.24)

\[ \Delta \omega_B^{(0)} = \left( \frac{t}{2\tau} \right) [z^2 + \theta^2 + \ldots] . \]  

(8.25)

These expressions are equal through terms of order \( t \) in the \( z \to 0 \) limit.

Since the sum of the roots of Eq. (7.1) is just \(-\xi\), there is a general relation between \( \Delta \omega_1 \) and \( \Delta \omega_B \) for the Eulerian fluid, namely

\[ \Delta \omega_1 + 2 \Delta \omega_B = - \tau R \sim = \tau^{-1} \theta \]  

(8.26)
Similar equations may be written for more complicated models as well. For example, Ref. 2 treated the reactive compressible fluid with the absence of diffusion. One can use the matrix \( Q \) in Eq. (4.7) of that paper to get

\[
\Delta \omega_o + \Delta \omega_1 + 2 \Delta \omega_B = - \text{tr} Q
\]

\[
= \tau^{-1} \theta + \nu k^2 [\kappa^* + (\eta_V + \frac{2}{3} \eta)]
\]

(8.27)

\[
\kappa^* = \kappa / C_{v,0}
\]

and \( \eta_V \) and \( \eta \) are the bulk and shear viscosities, respectively.

A further property of the roots is that their product is just the determinant of the matrix. Since \( \text{det} M = - z^2 \), we can thus express the displacement of the Brillouin peak, \( \omega_B \), by

\[
(\tau \omega_B)^2 = z^2 (\tau \Delta \omega_1)^{-1} - (\tau \Delta \omega_B)^2.
\]

(8.28)

This relationship can also be generalized.

Equations like (8.26) or (8.28), and their generalizations, present themselves as tests of experimental measurements to determine the applicability of a particular fluid model. Moreover, they provide an alternate computational method for characterizing the Brillouin peaks when the Rayleigh half-width expressions have previously been calculated in detail.

To consider Eqs. (8.24) and (8.25) in more detail, we define the function

\[
g(z) = 2t^{-1}(\tau \Delta \omega_B).
\]

(8.28)

Equation (8.26) may be used to show that

\[
g(z) = 1 - h(z).
\]

(8.29)
The behavior of \( g(z) \) is shown in Fig. 3 for both the \( t^- \) and \( z^- \) expansions.

It is known that in pure fluids experiencing normal transport processes, the Brillouin half-width is on the order of \( 10^7 \) sec\(^{-1}\). However, only for relaxation times \( \tau \) shorter than \( 10^{-10} \) sec do we begin to get such a half-width for the Eulerian model. This suggests that our description of \( \Delta \omega_B \) is inadequate, except possibly in the \( z \to 0 \) limit.

In order to more accurately assess the reactive contribution to the Brillouin half-width, one needs to use a more complete model of the system.

We now turn our attention to the cross section expressions in Eqs. (E.5) and (E.6). In contrast to the chemical reaction peak, the dominant term in \( R_B \) is \( \epsilon_p \), and in the \( z \to \infty \) limit, only pressure fluctuations at constant entropy and composition are important. This is expected if \( z \to \infty \) is regarded as a non-reactive limit. For small \( z \) on the other hand, there is a slight admixture of reaction dependence. The asymptotic values for the cross section are

\[
R_B^{(0)} \sim \frac{1}{2} \langle A/\theta \rangle \left[ \epsilon_p - \alpha \epsilon_\lambda \right]^2
\]

\[
\sim \frac{1}{2} \langle A/\theta \rangle \left[ c^-_o - \alpha \epsilon_\lambda \right]^2,
\]  \hspace{1cm} (8.30)

\[
R_B^{(\infty)} \sim \frac{1}{2} \langle A \rangle \epsilon_p^2
\]

\[
\sim \frac{1}{2} \langle A \rangle \left[ c^-_o - \epsilon_p \right]^2.
\]  \hspace{1cm} (8.31)

For systems having very small volume change and heat of reaction, \( \sigma \approx 0 \) and \( R_B \) will be just given by Eq. (8.31) over the whole domain of \( z \).
Displacement of the Brillouin Peak; Sound Speed Dispersion Relation.

We now turn to an analysis of the displacement of the Brillouin peak. This peak is shifted from $\omega = 0$ to a frequency $\omega_B$, whose $t$-expansion is

$$\omega_B = c_0 k \left\{ 1 - \frac{1}{8} t/s + (1/8)t^2 (3 - 6z^2 - z^4)/s^3 + \cdots \right\} . \tag{8.32}$$

The $z \to 0$ limit, on the other hand, is

$$\omega_B^{(o)} = c_\infty k \left\{ 1 + (1/8)z^2 (4 - t) t/\theta^3 + \cdots \right\} . \tag{8.33}$$

If we define a $z$-dependent sound speed by

$$V(z) \equiv \omega_B/k , \tag{8.34}$$

we see that Eqs. (8.32) and (8.33) give us a dispersion relation with $c_0$ as the short wavelength limit and $c_\infty$ as the long wavelength limit.

This dispersion has a simple physical basis. As a long wavelength phonon ($k << K$) moves through the scattering volume element, the variations induced by its passage are slow enough that the reaction equilibrium can follow them, hence the sound speed $c_\infty$. But for short wavelength phonons ($k >> K$), the variations occur so rapidly that equilibration of the reaction with each variation cannot obtain. Thus these large $k$ phonons propagate with the frozen sound speed $c_0$.

It is not necessary to use both Eq. (8.32) and Eq. (8.33) to describe $V(z)$. Since $t << 1$, we have the expansion
\[ \frac{c_e}{c_o} = \theta^{-\frac{1}{2}} = 1 - \frac{1}{8}t + (3/8)t^2 + \cdots \] (8.35)

and Eq. (8.32) in the \( z \to 0 \) limit gives

\[ V(o) = c_o \left[ 1 - \frac{1}{8}t + (3/8)t^2 + \cdots \right] = c_e. \] (8.36)

We conclude that, at least through terms of order \( t^2 \), Eq. (8.32) is valid in the entire \( z \) domain.

The range of dispersion, \( d \), of the sound speed is

\[ d = c_o - c_e \approx \frac{3}{8}c_o t, \] (8.37)

where Eq. (8.35) has been used. We define the "dispersion region" by the two values \( z_e \) and \( z_o \) such that

\[ V(z_e) = c_e + (1/10)d, \quad V(z_o) = c_o - (1/10)d. \] (8.38)

Solving these implicit relations, we find that \( z \) is in the dispersion region if

\[ \frac{3}{8} \leq z \leq 3. \] (8.39)

In Fig. 4 we have plotted \( V(z) \) in units of \( c_o \) using Eq. (8.32). The dispersion region defined by Eq. (8.39) has been indicated. For many \( z \) values of interest to us, we see that we will be able to interpret \( \omega_B \) simply as \( c_o k \) to a high degree of accuracy.

The type of dispersion mentioned here has been previously recognized in pure fluids and attributed to internal molecular relaxations. The analytical technique employed was to introduce a frequency-dependent bulk
viscosity, a technique common in ultrasonic analysis. We believe, however, that it is advantageous and more correct to introduce the relaxation process explicitly in the form of a chemical reaction equation as long as one is working at the hydrodynamic and thermodynamic level. Frequency dependent transport coefficients should be reserved to indicate non-Markovian memory effects in the hydrodynamic analysis.

Skewing of the Brillouin Peak

The presence of the small factor $\xi$ in Eq. (8.23) causes the Brillouin peak to be skewed from a Lorentzian shape. One of the effects of this is that the maximum intensity no longer occurs exactly at $\omega = \beta$ but is slightly shifted. Through first order in $\xi$ we find

$$\omega_B = \beta + \frac{1}{2} \xi \delta_B.$$  

(8.40)

Since $\xi$ may be either positive or negative, the peak maximum may be shifted in either direction. Figure 5 shows a graph of Eq. (8.23) with $\xi = 0$ (dotted line) and $\xi = 0.20$ (solid line).

When the peak is not pure Lorentzian, we may define two distinct "half-widths" in the following manner. We first calculate the frequencies $\omega_p$ and $\omega_m$ for which

$$S_B(\omega_m) = \frac{1}{2} S_B(\omega_B) = S_B(\omega_p).$$

(8.41)

Again through first order in $\xi$, the results are

$$\omega_p = \beta + \delta_B + \xi \delta_B, \quad \omega_m = \beta - \delta_B + \xi \delta_B.$$  

(8.42)
We then define the "half-widths" by

\[ \Delta \omega_p \equiv \omega_p - \omega_B = \delta_B + \frac{1}{2} \xi \delta_B , \]
\[ \Delta \omega_m \equiv \omega_B - \omega_m = \delta_B - \frac{1}{2} \xi \delta_B . \] (8.43)

Notice that the average value, \( \overline{\Delta \omega}_B \), of \( \Delta \omega_p \) and \( \Delta \omega_m \) is

\[ \overline{\Delta \omega}_B = \delta_B . \] (8.44)

This is just the value of \( \Delta \omega_B \) when \( \xi \) is zero.

As our quantitative measure of "skewness," we shall use the fractional difference of \( \Delta \omega_p \) and \( \Delta \omega_m \), which is zero when the peak is symmetrical. From Eqs. (8.43) and (8.44) we find

\[ \frac{\Delta \omega_p - \Delta \omega_m}{\Delta \omega_B} = \xi . \] (8.45)

We have previously referred to \( \xi \) as the "skewing factor" in anticipation of this very result.

Now that we have shown how \( \xi \) may be calculated from the experimental peak shape, we proceed to investigate the theoretical expressions for it, which are obtained from the calculation of \( P_\pm \). Using Eqs. (E.5) and (E.8) through terms of order \( t \), we have

\[ \xi = \frac{1}{2} (z/a^2) \xi_n / \xi_d \] (8.46)

where
\[ \xi_n = 4b(s-b) + t[(s+2) - 4b + b^2] + \cdots, \quad (8.47) \]

\[ \xi_d = [1 - 2b/s + b^2(1 - z^2)/s^2] \\
+ t[(1 - 4z^2)/s^2 - 2b(1 - z^2)/s^3 + b^2/s^2] + \cdots, \quad (8.48) \]

\[ b \equiv \alpha \varepsilon \lambda / \varepsilon \rho \]

We have again used the dimensionless number \( b \), which measures the relative importance of pressure and progress variable fluctuations.

In the \( z \to \infty \) limit, these expressions simplify considerably, and for \( z \) large enough that \( b \ll z \), we get

\[ \xi^{(\infty)} \sim \frac{1}{3}(4b + t)/z. \quad (8.49) \]

For completeness we include the expression for the small \( z \) limit,

\[ \xi^{(o)} \sim \frac{1}{3}z_0^{-3/2}(1 - b)^{-2}[3t + 2b(2 - t) - b^2(4 + t)]. \quad (8.50) \]

In Fig. 6 we have graphed \( \xi \) as a function of \( z \) with \( t = 10^{-3} \) and the indicated values of \( b \). Notice that the maximum of both curves lies very near \( z = 1 \). We have already seen in Fig. 4 that this same point lies in the region of strongest dispersion, and we recall the similar "dispersive" behavior of \( \Delta w_B \), \( \Delta w_1 \), and \( R_1 \) shown in Figs. 3, 1, and 2. This suggests that all these phenomena, including skewing, may have a physical origin similar to that for the sound speed dispersion.
In general, $\xi$ will be small enough that the effects of its presence may be neglected; e.g., in Eq. (8.40), we have $\xi \delta_B/\beta \approx 10^{-7}$, yet $\beta$ is perhaps only measured to one part in $10^5$. However, when line shape measurements become more precise, it may be of some interest to carry out similar calculations of $\xi$ on other fluid models.

9. QUANTITIES OF EXPERIMENTAL INTEREST

As a summary, and in order to fulfill the purpose of this article, we now distill the results of Section VIII into the observable characteristics of the spectrum of scattered light. For our Eulerian model, there are four peaks—two having the same frequency as the incident light, and two shifted to higher and lower frequencies by equal amounts. The first paragraph considers the ratios of intensities of these peaks. In the second paragraph is discussed the determination of the rate constant $\tau^{-1}$ by both direct and indirect means.

Intensities

Consider first the Landau-Placzek ratio

$$J_o = R_o/2R_B.$$  \hspace{1cm} (9.1)

Using the $z = 0$ expressions in Eqs. (E.6) and (E.9), we define the non-reactive limit by $\sigma = 0$ and $\Delta S = 0$. This results in the expression

$$J_o^{(o)} = (v/c_o)^2(C_{pS}o/T)(e_S/e_p)^2.$$  \hspace{1cm} (9.2)
If we now use Eq. (A.33), together with the assumption that $\tilde{e}_T = 0$, we get

$$J_1^{(o)} = (c_o/v)^2 \beta_o^2 T/C_{p,o} = (\gamma_o - 1).$$  \hspace{1cm} (9.3)

The second equality results from the identity in Eq. (A.14). Thus we have shown that at least the non-reactive contribution to the cross-section from the thermal peak is correct.

One may define a ratio $J_1$, which compares the total amount of light scattered into the reaction peak with that scattered into the Brillouin peaks, by

$$J_1 \equiv R_1/2R_B.$$

(9.4)

This is not an experimental quantity, although it could probably be extracted from the spectrum if it were possible to adequately resolve the observed Rayleigh peak into the sum of two Lorentzian shapes. The practical purpose of this calculation is that expressions for $J_1$ should make it possible to predict, in a qualitative fashion at least, the possibility of even observing the reaction peak.

We calculate first the $z \to 0$ limit of $J_1$. From Eqs. (E.3) and (E.6),

$$J_1^{(o)} \sim t^{-1} \left[ \frac{\alpha \epsilon + t \epsilon}{\epsilon + \alpha \epsilon} \right]^2. \hspace{1cm} (9.5)$$

In terms of the experimental $\epsilon$ derivatives (assuming $\tilde{e}_T = 0$), this is

$$J_1^{(o)} \sim t^{-1} \left[ \frac{\alpha \epsilon}{c_o - 2 \epsilon - \alpha \epsilon} \right]^2. \hspace{1cm} (9.6)$$
We see that there is a maximum value for $J_1$ when $\epsilon$ changes greatly during the conversion of reactants into products. In fact,

$$J_1^{(e)} \sim t^{-1}, \text{ if } c_o^2 \alpha \epsilon \lambda \gg \epsilon_p.$$  \hspace{1cm} (9.7)

Conversely, a weak dependence of $\epsilon$ upon $\lambda$ leads to the expression

$$J_1^{(e)} \sim v^2 c_o^2 \lambda^{-1}\left(\epsilon_\lambda/\epsilon_p\right)^2, \text{ if } c_o^2 \alpha \epsilon_\lambda \ll \epsilon_p.$$  \hspace{1cm} (9.8)

Considering now the $z \to \infty$ limit of $J_1$, Eqs. (E.2) and (E.5) may be combined to give

$$J_1^{(e)} \sim t^{-1}(\alpha \epsilon_\lambda/\epsilon_p)^2.$$  \hspace{1cm} (9.9)

If we again assume $\bar{\epsilon}_T = 0$, we can write

$$J_1^{(e)} \sim v^2 c_o^2 \lambda^{-1}\left(\epsilon_\lambda/\epsilon_p\right)^2.$$  \hspace{1cm} (9.10)

This is to be contrasted with Eq. (9.8). The implications of Eq. (9.10) are clear. The greater the change in $\epsilon$ due to reaction, the more intense will the reaction peak be. The inverse dependence on $\lambda$ is also quite appropriate. One feels intuitively that if $\lambda$ (the curvature of $\Delta G$ along the reaction coordinate in the neighborhood of equilibrium) is small, then the composition may make relatively large fluctuations around its equilibrium value. The corresponding fluctuations of $\epsilon$ will be large and hence more light will be scattered by this mode.

Immediate contact between theory and experiment may be made by comparing the total Rayleigh intensity to the Brillouin intensity,

$$J \equiv \left(R_0 + R_1\right)/2R_B.$$  \hspace{1cm} (9.11)
We calculate this in the \( z \to \infty \) limit. Use of Eqs. (E.1), (E.2), and (E.5) results in the expression

\[
J^{(\infty)} = Q^{-1} (C_{p, o}/T) \left\{ \frac{\varepsilon \frac{2}{\mathcal{C}_{p, o}} \Lambda + 2 \varepsilon \frac{2}{\mathcal{C}_{\lambda}} T \Delta S + T \varepsilon_p^2}{(c_o/\nu)^2 \varepsilon_p^2} \right\}.
\]  

(9.12)

Employing the relation \( C_{p, o} \Lambda = Q + T (\Delta S)^2 \), and then using Eq. (A.33) with \( \varepsilon_T = 0 \), gives the apparently complicated form

\[
J^{(\infty)} = (c_o/\nu)^2 \frac{2}{\mathcal{C}_{p, o}} T \frac{2}{\mathcal{C}_{p, o}} \left[ \frac{(v^{-1} + \frac{2}{\mathcal{C}_{p, o}} T \Delta S / v^2 \varepsilon_p)}{\varepsilon_p} + \varepsilon_{\lambda} \right]^2. 
\]  

(9.13)

From Eq. (A.14), we identify the first term as \( (v_o - 1) \), the non-reactive limit of \( J \). We can use Eqs. (A.19) and (A.22) to write

\[
v^{-1} + \frac{2}{\mathcal{C}_{p, o}} T \Delta S / v^2 = \varepsilon_{\rho} = \rho^2 \Delta v.
\]  

(9.14)

Thus, we have

\[
J^{(\infty)} = (v_o - 1) + v^2 \frac{2}{\mathcal{C}_{p, o}} Q^{-1} \left[ (\rho^2 \Delta v / \varepsilon_{\rho} + \varepsilon_{\lambda}) / \varepsilon_{\rho} \right]^2.
\]  

(9.15)

Finally, we consider a ratio which may be more useful than \( J_1 \) for predicting the possibility of observing the reaction peak. Though \( J_1 \) may be large for a given system, the reaction peak may be so broad that it is hardly discernible from the background. Thus, we calculate \( \tilde{J}_1 \), the ratio of maximum intensities of the reaction and Brillouin peaks,

\[
\tilde{J}_1 = \frac{S_{1, \text{max}}}{S_{B, \text{max}}}.
\]  

(9.16)
For comparison with Eq. (9.6), we find in the $z \to 0$ limit

\[ \tilde{J}_1^{(\infty)} \sim \frac{\theta}{\theta^3} \left[ -\frac{\alpha \epsilon \lambda}{c_o - \theta \epsilon \rho - \alpha \epsilon \lambda} \right]^2, \tag{9.17} \]

while in the $z \to \infty$ limit

\[ \tilde{J}_1^{(\infty)} \sim \left( \frac{\alpha \epsilon \lambda}{\epsilon \rho} \right)^2. \tag{9.18} \]

If we compare $\tilde{J}_1^{(\infty)}$ with $J_1^{(\infty)}$, we see that $J_1^{(\infty)}$ does not depend on $\sigma$ while $\tilde{J}_1^{(\infty)}$ does.

We note here that since the $M_j$ are projection matrices,

\[ \sum_j M_j = I, \]

and using this in Eqs. (3.20), we can derive the sum rule

\[ \int_{-\infty}^{+\infty} S(k,\omega) d\omega = 2\pi (\partial \epsilon / \partial x)^\sigma \cdot G \cdot (\partial \epsilon / \partial x)^\sigma. \]
Determination of $\tau^{-1}$

In this article we have emphasized the use of light scattering as a tool for the study of fast reactions. The major effect of the chemical reaction is the addition of a second Rayleigh peak to the spectrum. The half-width of this peak has the angular dependence

$$
\Delta \omega_1 = a + b_1/(b_2 + k^2).
$$

(9.19)

The constant $a$ is to be interpreted as $\tau^{-1}$, the rate of relaxation of the reaction toward equilibrium at constant entropy and pressure. This is related to the rate constant at constant temperature and pressure by

$$
\tau_{T,p}^{-1} = \tau^{-1}[1 - T(\Delta S)^2/C_{p,s} \cdot \Lambda].
$$

(9.20)

The term in brackets is normally very close to unity. The constants $b_1$ and $b_2$ have the meanings

$$
b_1 = \tau^{-1} k^2, \quad b_2 = k^2,
$$

(9.21)

where $K = (\tau c_0)^{-1}$. The value of $c_0$ is furnished by the Brillouin peak displacement.
There is a potential difficulty in data analysis due to the presence of the thermal peak, whose half-width is

\[ \Delta \omega_0 = (\nu \kappa / C_p \varepsilon) k^2 + \cdots . \tag{9.22} \]

Assuming a thermal conductivity on the order of \(10^{-4}\) cal/sec-cm-deg, we may estimate \(\Delta \omega_0\) to be on the order of \(10^5-10^6\) sec\(^{-1}\). To easily separate the two peaks, then, requires us to consider reaction times less than \(10^{-7}\) sec or greater than \(10^{-4}\) sec. Of course, if \(\tau\) is too short, the reaction peak will be so wide as to either overlap the Brillouin peaks, or be too weak to be detected. The latter conclusion results from noting that

\[ S_1^{\text{max}} = R_1 / \Delta \omega_1 \approx \tau R_1 . \]

For intermediate times (e.g., \(\tau \approx 10^{-4}-10^{-6}\) sec), one must study the angular dependence of the Rayleigh peak and extract \(\Delta \omega_0\) and \(\Delta \omega_1\) by curve fitting procedures.

Under certain circumstances, namely,

(1.) small volume change and heat of reaction,
(2.) small dependence of \(\varepsilon\) on \(\lambda\),
(3.) large dependence of \(\Delta G\) on \(\lambda\),
(4.) very short relaxation time,

the chemical reaction peak will be too weak to be of any value. It may still be possible to obtain \(\tau^{-1}\) from the analysis of other spectral
characteristics. In particular, when very fast reactions are involved 
($\tau \leq 10^{-9}$ sec), adequate information to calculate $\tau^{-1}$ may be found in
the dispersion relation

$$V(k) = c_0 - \frac{b_1}{(b_2 + k^2)}, \quad z \approx 1,$$  \hspace{1cm} (9.23)

where $c_0$ is the high-frequency limit of the sound speed, and

$$b_1 = \frac{3}{8} c_0 \left( \frac{\tau c_0}{\tau c_0} \right)^{-2}, \quad b_2 = \left( \frac{\tau c_0}{\tau c_0} \right)^{-2}.$$  \hspace{1cm} (9.24)

In the limit of small angle scattering,

$$V(k) = c_e + a k^2 , \quad z \ll 1$$  \hspace{1cm} (9.25)

where the constant $a$ is

$$a = \frac{1}{3} c_e \left( \frac{\tau c_0}{\tau c_0} \right)^2$$  \hspace{1cm} (9.26)

and $c_e$ is the low-frequency limit of the sound speed. Equations (9.23)
and (9.26) are also valid for very small scattering angles.
10. CONCLUSIONS

In closing we make three remarks about our calculation. First, we note the advantages of the matrix formulation. Once the matrix $M$ has been constructed, its eigenvalue problem may be solved by any of a number of methods. The entire spectral distribution of scattered light follows immediately from the eigenvalues $\zeta_j$ by way of Eqs. (6.10a) and (6.10c). The cross section due to relaxation of the $j$-th normal mode is easily expressed in terms of $\zeta_j$ by using the projection matrix $M_j$. Also, we recall the half-width and displacement information contained in the trace and determinant of $M$.

Second, we note that the relaxation time of the chemical reaction furnishes a natural time scale for the processes occurring in the scattering system. Although this was implicit in the scaling of the eigenvalue problem, it found explicit expression in the occurrence of the dimensionless variable $z = \tau c_0 k$. It will be remembered that $z$ served not only as a comparator of the two relaxation times, $\tau$ and $(c_0 k)^{-1}$, in the interpretation of the small and large $z$ limits, but also as a comparator of the two wave-numbers, $(\tau c_0)^{-1}$ and $k$, in the discussion of the sound speed dispersion.

In conclusion, our calculations seem to be appropriate for the analysis of fast reactions by light scattering measurements, and they can probably be considered good first approximation results for observing reactions with rates in the range $10^4 - 10^{11}$ sec$^{-1}$. We question the immediate applicability of our results to ionic reactions, since charge relaxation by
diffusion as well as reaction can be a significant effect which we have ignored. In general, our model is most representative of fluids with small thermal conductivities, diffusion coefficients, and viscosities, and for reactions between neutral species.
APPENDIX A: THERMODYNAMIC NOTATION AND RELATIONS

The thermodynamic state of a system may be completely described by the potential

\[ H = H(S, p, m) \]  \hspace{1cm} (A.1)

and the corresponding Gibbsian differential

\[ dH = T \, dS + V \, dp + \mu \cdot dm . \]  \hspace{1cm} (A.2)

\( H \) is the enthalpy of the system, \( S \) the entropy, \( V \) the volume, \( T \) the temperature, and \( p \) the pressure. The \( c \)-vector \( m = \{ m_1, \ldots, m_c \} \) specifies the mass of each of the \( c \) species present, and \( \mu = \{ \mu_1, \ldots, \mu_c \} \) denotes the specific chemical potentials of all the species.

An arbitrary number, \( n \), of independent chemical reactions are represented by chemical equations of the form

\[ \sum_{s} v_s^\alpha x_s = 0 , \quad (\alpha = 1, 2, \ldots, n) \]  \hspace{1cm} (A.3)

where \( x_s \) represents unit mass of species \( s \), and \( v_s^\alpha \) is the specific stoichiometric coefficient for species \( s \) in the \( \alpha \)-th reaction. The equations are written for the transformation of a unit mass of reactants (negative \( v_s^\alpha \)) to a unit mass of products (positive \( v_s^\alpha \)). Thus,

\[ \sum_{s \text{ reactants}} v_s^\alpha = -1 , \quad \sum_{s \text{ products}} v_s^\alpha = +1 . \]
Each reaction is characterized by its progress variable $\lambda_{\alpha}$, which is defined such that the increment produced in the mass fraction, $w_s$, of species $s$ by all the reactions is

$$dw_s = \sum_{\alpha} v_s^\alpha d\lambda_{\alpha},$$  \hspace{1cm} (A.4)

$$w_s = \frac{m_s}{\sum_t m_t}.$$  

Rates of reaction are defined by

$$\dot{r} = \frac{d\lambda}{dt},$$  \hspace{1cm} (A.5)

where $\lambda = \{\lambda_1, \ldots, \lambda_n\}$, and $r = \{r_1, \ldots, r_n\}$ are the rates of the $n$ chemical reactions. The rate $r_{\alpha}$ is assumed to be a known function of the local thermodynamic state.

In this article, the independent variables chosen to describe a general thermodynamic state are $S$, $p$, and $\lambda$. The fundamental equation (for unit mass) is

$$dH = T \, ds + v \, dp + \Delta G \cdot d\lambda,$$  \hspace{1cm} (A.6)

where $H$, $S$, and $v$ are specific quantities, and

$$\Delta G = \{\Delta G_1, \ldots, \Delta G_n\} = (\frac{\partial G}{\partial \lambda})_{T, p, \lambda'} = (\frac{\partial H}{\partial \lambda})_{S, p, \lambda'},$$  \hspace{1cm} (A.7)

$$\Delta G_{\alpha} = \sum_s v_s^\alpha \mu_s = (\frac{\partial G}{\partial \lambda_{\alpha}})_{T, p, \lambda'}.$$  

The subscript $\lambda'$ denotes all $\lambda$'s except the one involved in differentiation,
G is the Gibbs free energy, and $\Delta G_A$ is the Gibbs free energy increment due to reaction $\alpha$. Also associated with the chemical reactions are the following functions:

heats of reaction

$$\Delta H = \sum_{\lambda} \bar{h} = \left( \frac{\partial H}{\partial \lambda} \right)_{T, P, \lambda} , \quad (A.8a)$$

and volume increments of reaction

$$\Delta V = \sum_{\lambda} \bar{V} = \left( \frac{\partial V}{\partial \lambda} \right)_{T, P, \lambda} . \quad (A.8b)$$

In these definitions, $\bar{h} = \{ \bar{h}_1, \ldots, \bar{h}_c \}$, $\bar{V} = \{ \bar{V}_1, \ldots, \bar{V}_c \}$, and $\gamma$ is the $n \times c$ matrix $\{ \gamma_{s}^{\alpha} \}$. $\bar{h}_s$ is the partial specific enthalpy of species $s$, and $\bar{V}_s$ the partial specific volume.

A relation which will be useful in the thermodynamic calculations is

$$d\Delta G = \left( \frac{\partial \Delta G}{\partial S} \right)_{P, \lambda} dS + \left( \frac{\partial \Delta G}{\partial p} \right)_{S, \lambda} dp + \left( \frac{\partial \Delta G}{\partial \lambda} \right)_{S, P, \lambda} \Lambda d\lambda$$

$$= \left( \frac{\partial T}{\partial \lambda} \right)_{S, P, \lambda} dS + \left( \frac{\partial V}{\partial \lambda} \right)_{S, P, \lambda} dp + \Lambda d\lambda , \quad (A.9)$$

$$\Lambda = \left( \frac{\partial \Delta G}{\partial \lambda} \right)_{S, P, \lambda} , \quad \Lambda_{\alpha \beta} = \left( \frac{\partial^2 H}{\partial \lambda_{\alpha} \partial \lambda_{\beta}} \right)_{S, P, \lambda} .$$

The second equality follows from Eq. (A.6).
"Frozen" and "Equilibrium" Derivatives

There is a general class of "frozen" thermodynamic coefficients defined as derivatives taken at constant \( \lambda \), and another class of "equilibrium" thermodynamic coefficients defined as derivatives taken at constant \( \Delta G \) and evaluated at \( \Delta G = 0 \). The relation between the two sets is established with the help of a well-known relation from differential calculus. Consider a general thermodynamic function \( Y \) in terms of two sets of independent variables

\[
Y = Y(S, p, \lambda) \quad \text{and} \quad Y = Y(S, p, \Delta G).
\]

The general relation between frozen and equilibrium derivatives is shown by the following example:

\[
\left( \frac{\partial Y}{\partial p} \right)_{S, \Delta G} = \left( \frac{\partial Y}{\partial p} \right)_{S, \lambda} + \left( \frac{\partial Y}{\partial \lambda} \right)_{S, p, \lambda} \cdot \left( \frac{\partial \lambda}{\partial p} \right)_{S, p, \lambda} \cdot \Delta G \ \ (A.10)
\]

Now, from Eq. (A.9),

\[
d\lambda = - \lambda^{-1} \left( \frac{\partial \lambda}{\partial S} \right)_{S, p, \lambda} \ dS - \lambda^{-1} \left( \frac{\partial \lambda}{\partial p} \right)_{S, p, \lambda} \ dp
\]

\[
+ \lambda^{-1} \ d\Delta G, \ \ (A.11)
\]

so that

\[
\left( \frac{\partial Y}{\partial p} \right)_{S, \Delta G} = \left( \frac{\partial Y}{\partial p} \right)_{S, \lambda} - \left( \frac{\partial Y}{\partial \lambda} \right)_{S, p, \lambda} \cdot \lambda^{-1} \left( \frac{\partial \lambda}{\partial p} \right)_{S, p, \lambda} \ \ (A.12)
\]

Frozen coefficients are denoted by a subscript zero, equilibrium coefficients by a subscript e.
The frozen coefficients considered in this article are

\[ C_{p,0} = \left( \frac{\partial H}{\partial T} \right)_{p,0} = T \left( \frac{\partial S}{\partial T} \right)_{p,0}, \]  
(A.13a)

\[ C_{v,0} = \left( \frac{\partial E}{\partial T} \right)_{v,0} = T \left( \frac{\partial S}{\partial T} \right)_{v,0}, \]  
(A.13b)

\[ \gamma_0 = \frac{C_{p,0}}{C_{v,0}}, \]  
(A.13c)

\[ \beta_0 = \left( \frac{\partial v}{\partial T} \right)_{p,0}, \]  
(A.13d)

and the frozen sound speed, \( c_0 \), obtained from

\[ c_0^2 = -\nabla^2 \left( \frac{\partial \rho}{\partial v} \right)_{S,0} = \nabla^2 \frac{c_{p,0}(\gamma_0 - 1)}{T \beta_0^2}. \]  
(A.14)

An important equilibrium coefficient is the equilibrium sound speed,

\[ c_e^2 = -\nabla^2 \left( \frac{\partial \rho}{\partial v} \right)_{S,\Delta G}. \]  
(A.15)

Properties of the Chemical Reactions

The most useful way of discussing chemical reactions and the increments associated with them is to use the equation

\[ \frac{d\Delta G}{\Delta T} = \Delta S \frac{dT}{\Delta T} + \Delta v \frac{dp}{\Delta p} + \frac{\Lambda_T}{\Delta \lambda} \frac{d\lambda}{\Delta \lambda}, \]

\[ \Lambda_T = \left( \frac{\partial \Delta G}{\partial \lambda} \right)_{T, p, \lambda}. \]  
(A.16)

The coefficients in Eq. (A.9) may now be related to the increments in Eq. (A.16). For example,
\[
\left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} = \left(\frac{\partial \Delta G}{\partial p}\right)_{S,\lambda}
\]

\[
= - \Delta S \left(\frac{\partial T}{\partial p}\right)_{S,\lambda} + \Delta v \quad .
\] (A.17)

Use of the Maxwell relation

\[
\left(\frac{\partial T}{\partial p}\right)_{S,\lambda} = \left(\frac{\partial v}{\partial S}\right)_{p,\lambda} = \left(\frac{\partial v}{\partial T}\right)_{p,\lambda} \left(\frac{\partial T}{\partial S}\right)_{p,\lambda} = \beta_o T/C_{p,o}
\] (A.18)

yields

\[
\Delta v = \left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} + \left(\frac{\partial \Delta G}{\partial \lambda}\right)_{S,P,\lambda'} \Delta S \quad .
\] (A.19)

It is convenient to associate with the chemical reactions a vector \(\mathbf{v}_o\), defined by

\[
\mathbf{v}_o = \Delta v - (\beta_o/C_{p,o}) \Delta H \quad .
\] (A.20)

Using Eq. (A.19), this becomes

\[
\mathbf{v}_o = \left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} - (\beta_o/C_{p,o}) \Delta G \quad ,
\] (A.21)

and at a point of chemical equilibrium,

\[
\left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} = \mathbf{v}_o \quad .
\] (A.22)

The frozen and equilibrium sound speeds may be related by use of Eqs. (A.12) and (A.22):

\[
\left(\frac{\partial v}{\partial p}\right)_{S,A} = \left(\frac{\partial v}{\partial p}\right)_{S,\lambda} - \left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} \Delta^{-1} \left(\frac{\partial v}{\partial \lambda}\right)_{S,P,\lambda'} \quad ,
\]
and evaluating this at \( \Delta G = 0 \),

\[
\frac{c_e}{c_o}^2 = \left( 1 + \frac{c_o}{c_e} \right) \text{e}^{\sigma \cdot \Lambda^{-1} \cdot \sigma}. \tag{A.23}
\]

Chemical Stability

The second law of thermodynamics may be used to show that at a point of chemical equilibrium (\( \lambda = \lambda_e \)) in a closed system at constant \( S \) and \( p \), the enthalpy must be a minimum. Since

\[
\mathcal{H}(S, p, \lambda) = \mathcal{H}(S, p, \lambda_e) + \Delta G \cdot \delta \lambda + \frac{1}{2} \delta \lambda \cdot \Lambda \cdot \delta \lambda + \ldots
\]

and \( \Delta G = 0 \) at equilibrium, then

\[
\mathcal{H} - \mathcal{H}_e = \frac{1}{2} \delta \lambda \cdot \Lambda \cdot \delta \lambda > 0 \tag{A.24}
\]

Thus, the symmetric matrix \( \Lambda_e \) is positive definite.

Chemical Rate Functions

Near chemical equilibrium, the rate functions may be expanded in powers of the free energy increments, which are the driving forces for reaction. Considering only linear terms,

\[
\mathfrak{r} = -L \cdot \Delta G + \ldots \tag{A.25}
\]

From the theory of irreversible thermodynamics and the Onsager reciprocal relations, \( L \) is known to be a real, symmetric, positive definite matrix.
In order to relate $r$ to the independent variables, $\Delta G$ itself is expanded in powers of $(\lambda - \lambda_e)$. To linear terms,\(^{22}\)

$$
\Delta G = \Lambda_e (\lambda - \lambda_e), \quad (A.26)
$$

and the rate laws have the form

$$
d\lambda/dt = r(S,p,\lambda) = \Omega^*(\lambda - \lambda_e), \quad (A.27)
$$

where $\Omega = -L^*\Lambda_e$. The spectrum of $\Omega$ determines the relaxation times for the reactions.

One Reaction Case

When there is only one reaction, we define its relaxation time by

$$
\tau_{S,p} \equiv -\Omega^{-1} = (L\Lambda_e)^{-1}, \quad (A.28)
$$

where the subscripts indicate that this relaxation time is measured at constant $S$ and $p$. Equation (A.12) may be used to show that

$$
\tau_{S,p} = \theta \tau_{S,v},
$$

$$
\theta = 1 + c_0^2 \sigma^2 / \Lambda. \quad (A.29)
$$

The calculation of $\Lambda$ follows a standard procedure.\(^{17}\) From Eq. (A.7),

$$
\Lambda = (\partial \Delta G/\partial \lambda)_{S,p} = \sum v_S (\partial \mu_S/\partial \lambda)_{S,p} \quad (A.30)
$$
For ideal solutions,

\[ \mu_s = \mu_s^0 + \frac{(RT/M)}{\ln \omega_s} \]  

(A.31)

where R is the gas constant and M is the number of grams per mole of the system. Taking the derivative of \( T \ln \omega_s \) with respect to \( \lambda \), we find

\[ \Lambda = \frac{(RT/M)}{\sum_s \omega_s [(\psi_s/\psi_s) - (\Delta S/C_{p,0}) \ln \omega_s]} \]  

(A.32)

**Derivatives of \( \varepsilon \)**

In this article we use the following thermodynamic derivatives of \( \varepsilon \):

\[ \varepsilon_S \equiv \frac{\partial \varepsilon}{\partial S}_{p,\lambda}, \quad \varepsilon_p \equiv \frac{\partial \varepsilon}{\partial p}_{S,\lambda}, \quad \varepsilon_\lambda \equiv \frac{\partial \varepsilon}{\partial \lambda}_{S,p} \]

For the sake of utility, we give here the relations connecting these derivatives to the more common experimental ones

\[ \bar{\varepsilon}_T \equiv \frac{\partial \varepsilon}{\partial T}_{\rho,\lambda}, \quad \bar{\varepsilon}_\rho \equiv \frac{\partial \varepsilon}{\partial \rho}_{T,\lambda}, \quad \bar{\varepsilon}_\lambda \equiv \frac{\partial \varepsilon}{\partial \lambda}_{T,\rho} \]

where \( \rho = 1/\nu \) is the density. The equations are

\[
\begin{pmatrix}
\varepsilon_S \\
\varepsilon_p \\
\varepsilon_\lambda
\end{pmatrix}
= \begin{pmatrix}
T/C_{p,0} & \frac{\beta_o T}{\nu} & \varepsilon_{T}
\\
\frac{\beta_o T}{C_{p,0}} & \frac{1}{\nu C_o^2} & \varepsilon_p
\\
\frac{-T \Delta S}{C_{p,0}} & -\frac{\rho}{\nu} & \varepsilon_\lambda
\end{pmatrix}
\]

(A.33)

A common simplification of these equations, which we shall have occasion to use, is the assumption that \( \bar{\varepsilon}_T = 0 \).
APPENDIX B: THE CORRELATION FUNCTION

In the calculation of $G = \langle a(k,0)a(-k,0) \rangle$ in Section V, there appears the integral

$$U(k) = \int_{-\infty}^{\infty} v(R) \exp(-ik \cdot R) dR.$$ 

Since we have assumed $v$ depends only on the magnitude of $R$, we can do the angular integrations to get

$$U(k) = \frac{4\pi}{k} \int_{0}^{\infty} v(R) R \sin kR dR$$  \hspace{1cm} (B.1)$$

We have written $U$ and $v$ as scalars here, due to Eq. (5.6). Now, on the coarse-grained thermodynamic scale used to define $v(R)$, we expect correlations to decay in a monotonic fashion. We assume the functional form

$$v(R) = e^{-\frac{R}{R_c}},$$  \hspace{1cm} (B.2)$$

where $R_c$ is a measure of the "range" of correlation. Substituting this into Eq. (B.2) and integrating gives

$$U(k) = 4\pi R_c^3 (1 + k^2 R_c^2)^{-2}.$$  \hspace{1cm} (B.3)$$

Since we have assumed $kR_c << 1$, this may be expanded to give

$$U(z) = 3V_c [1 - 2(R_c^2 k^2)z^2 + \ldots]$$  \hspace{1cm} (B.4)$$

where $V_c = \frac{4}{3} \pi R_c^3$ is a "characteristic volume" for $v(R)$, and $K = (\tau c_0)^{-1}$ is a "characteristic wave number" for the system.
Effect of the k-Dependence of $U(k)$

To see the effect of the $z^2$ term in Eq. (B.4) on the behavior of $P_j$, we simply multiply together the $z$-expansion of $P_j$, for example $P_1$, and the term in brackets in Eq. (B.4). Using Eq. (E.2) for $R_1^{(o)}$ we see that we must compare

$$2(R_c 2K^2)(\alpha_{\lambda} t + t_{P})^2 \text{ with } 2\varepsilon (\alpha_{\lambda} t + t_{P})t/\theta^2.$$ Consider the coefficient of $t^2\varepsilon_{P}^2$, we see that the k-dependence of $U$ becomes important if

$$R_c 2K^2 \approx 1.$$

(B.5)

For $N_2O_4$, we have $K \approx 10^{-2} \text{ cm}^{-1}$, so we would need to have a range of correlation of nearly 100 cm for the k-dependence of $U$ to be significant. This calculation thus indicates that the k-dependence of $G$ is justifiably ignored.
APPENDIX C: THERMODYNAMIC FLUCTUATION THEORY

Making a straightforward extension of the formulas of Landau and Lifshitz\textsuperscript{23} to include chemical reaction, we get the probability of observing a fluctuation in the volume element $V_c$ as

$$w(\hat{x}) = A \exp \left[ -\frac{1}{2k_B T} \left( \frac{V_c}{v} \right) X \psi^2 \right]$$

$$\times \exp \left[ -\frac{1}{2k_B T} \left( \frac{V_c}{v} \right) (\hat{\Delta} - \hat{p} \hat{v} + \Delta \hat{\lambda}) \right]. \quad (C.1)$$

In this equation, $k_B$ is Boltzmann's constant, and $X$ is an unknown coefficient for fluctuations in $\psi$. The assumption has been made that fluctuations in $\psi$ are independent of those in the thermodynamic variables.\textsuperscript{13a}

Important in Eq. (C.1) is the ratio $(V_c/v)$, which is the number of grams of material in the volume element. This factor arises because we are calculating a fluctuation in a volume $V_c$ using thermodynamic variables which are specific, i.e. per unit mass. In addition to converting units, this factor also assures us that the mean square fluctuations will be inversely proportional to $V_c$.

The independent thermodynamic variables have been taken to be $S$, $p$, and $\lambda$, and the equations governing their fluctuations have been solved in Section IV. Fluctuations in other variables, for example $T$, may be expressed as

$$\hat{T} = \left( \frac{\partial T}{\partial S} \right)_p \hat{S} + \left( \frac{\partial T}{\partial p} \right)_S \hat{p} + \left( \frac{\partial T}{\partial \lambda} \right)_S \hat{\lambda} + \cdots. \quad (C.2)$$
Expanding \( v \) and \( G \) in similar fashion, we may put Eq. (C.1) into the form

\[
w(\hat{x}) = A \exp\left(-\frac{V_c}{2\nu k_B T}T^{-1}\lambda \psi^2 + T^{-1}(\partial T/\partial S)_{p,\lambda} S^2 + 2T^{-1}(\partial T/\partial \lambda)_{S,p} \hat{S}\lambda - T^{-1}(\partial V/\partial p)_{S,\lambda} \hat{p}^2 + T^{-1}(\partial \Delta G/\partial \lambda)_{S,p} \hat{\lambda}^2\right].
\]

(C.3)

Expressing the quadratic form in the exponent in matrix notation, we have

\[
w(\hat{x}) = A \exp[-(V_c/2\nu k_B) \hat{x} \cdot E \cdot \hat{x}],
\]

(C.4)

where \( E \) is the symmetric matrix

\[
E = T^{-1} = \begin{pmatrix} (\partial T/\partial S)_{p,\lambda} & 0 & 0 & (\partial T/\partial \lambda)_{S,p} \\ 0 & X & 0 & 0 \\ 0 & 0 & -(\partial V/\partial p)_{S,\lambda} & 0 \\ (\partial T/\partial \lambda)_{S,p} & 0 & 0 & (\partial \Delta G/\partial \lambda)_{S,p} \end{pmatrix}.
\]

(C.5)

and \( A \) is a normalization constant such that

\[
\int w(\hat{x}) \, d\hat{x} = 1.
\]

(C.6)

The dyadic \( \langle \hat{x}\hat{x} \rangle \) is easily calculated by the method of de Groot and Mayer.\(^{12}\) Introduce the vector \( \gamma \) by
$$y \equiv (v_{B}/v_{c})(\partial L_{n}w/\partial \hat{x}) = (v_{B}/v_{c})^{-1}(\partial w/\partial \hat{x}) . \quad (C.7)$$

From Eq. (C.4) this may also be written

$$y = -E \cdot \hat{x} . \quad (C.8)$$

Now, the average value of $y\hat{x}$ is

$$\langle y\hat{x} \rangle = \int_{-\infty}^{\infty} y\hat{x} w(\hat{x})d\hat{x} = (v_{B}/v_{c}) \int_{-\infty}^{\infty} \hat{x}(\partial w/\partial \hat{x})d\hat{x} . \quad (C.9)$$

Partial integration of the second integral gives

$$\langle y\hat{x} \rangle = -(v_{B}/v_{c}) \int \hat{x}(\partial \hat{x}/\partial \hat{x})d\hat{x} . \quad (C.10)$$

Inasmuch as the components of $\hat{x}$ are all independent, however, the quantity $(\partial \hat{x}/\partial \hat{x})$ is just the unit dyadic $I$. Thus,

$$\langle y\hat{x} \rangle = -(v_{B}/v_{c}) \int w(\hat{x})d\hat{x} = -(v_{B}/v_{c})I , \quad (C.11)$$

where Eq. (C.6) has been used. From Eq. (C.8) for $y$, we get the desired form,

$$\langle \hat{x}\hat{x} \rangle = (v_{B}/v_{c})^{-1} . \quad (C.12)$$
APPENDIX D: EVALUATION OF THE MATRIX FUNCTIONS $F_j(B)$

Since the calculation of the matrices $F_j(B)$ is somewhat complicated, we outline the procedure here. Referring to Eqs. (4.16) and (4.9), we have

\[
B = \begin{bmatrix}
0 & 0 \\
B_{21} & B_{22}
\end{bmatrix},
\]

with

\[
B_{21} = \tau M_{21}, \quad B_{22} = \tau M_{22}.
\]

Since all powers of $B$ will have the same block structure, we find from Eq. (4.23)

\[
F_0(B) = \begin{bmatrix}
z^2 & 0 \\
\nu_0 & F_0(B_{22})
\end{bmatrix}.
\]

We note that $F_0(\zeta)$ is the characteristic polynomial of $B_{22}$, and hence, by Cayley's theorem, $F_0(B_{22}) = 0$. The column vector $\nu_0$ is given by

\[
\nu_0 = g_0(B_{22}) \cdot B_{21},
\]

\[
g_0(\zeta) = \zeta^2 + \theta \zeta + z^2.
\]
Using the explicit form of $M_{22}$ given in Eq. (4.11), we find

$$g_{\omega}(B_{22}) = \begin{pmatrix} 0 & -\tau v k^2 & \tau^{-1} \sigma z^2 \\ \tau c_0^2 / v & 0 & 0 \\ -\tau c_0^2 L\sigma & 0 & z^2 \end{pmatrix}. \quad (D.5)$$

Thus,

$$V_{\omega} = \begin{pmatrix} 0 \\ 0 \\ z^2 \tau TL\Delta S/C_{p_{\omega}} \end{pmatrix}. \quad (D.6)$$

Combining these results we obtain the form of $F_{\omega}(B)$ given in Eqs. (4.27) and (4.28).

Using the expression in Eq. (4.24) for $F_j(\zeta)$, we have

$$F_{j}(B) = \begin{pmatrix} 0 & 0 \\ V_j & F_{j}(B_{22}) \end{pmatrix}, \quad (D.7)$$

where

$$V_j = g_{\omega}(B_{22}) \cdot B_{21}, \quad g_{\omega}(\zeta) = \zeta^2 + (\theta + \zeta_j)\zeta + (\zeta_j^2 + 3\zeta_j + z^2). \quad (D.8)$$
Recalling the definition of $g_o$ in Eq. (D.4), we may write

$$g_j(\zeta) = g_o(\zeta) + \zeta_j \zeta + (\zeta_j^2 + \theta \zeta_j) ,$$  \hspace{1cm} (D.9)

which is convenient, since we already have $g_o(B_{22})$ in Eq. (D.5).

Calculation of $V_j$ gives

$$V_j = \begin{pmatrix} -\zeta_j \frac{z^2}{\zeta} \\ \zeta_j^2 c_o \frac{2}{\sigma / v} \\ \zeta_j^2 + z^2 \end{pmatrix}.$$  \hspace{1cm} (D.10)

To evaluate $F_j(B_{22})$, we write the function in the form

$$F_j(\zeta) = F_o(\zeta) + \zeta_j \zeta^2 + (\zeta_j \theta + \zeta_j^2) \zeta - z^2 .$$  \hspace{1cm} (D.11)

Since $F_o(B_{22}) = 0$, we may write

$$F_j(B_{22}) = \zeta_j B_{22}^2 + (\zeta_j \theta + \zeta_j^2) B_{22} - z^2 I .$$  \hspace{1cm} (D.12)

Evaluating this expression explicitly gives

$$F_j(B_{22}) = \begin{pmatrix} -z^2(1+\zeta_j) & -\tau v k^2 \zeta_j(1+\zeta_j) & \zeta_j z^2 \sigma / \tau \\ \zeta_j^2 c_o \frac{2}{\zeta} -z^2(1+\zeta_j) - (\theta-1) \zeta_j^2 & -\zeta_j^2 c_o \frac{2}{\sigma / v} \\ -\zeta_j^2 c_o \frac{2}{\zeta} -\tau v L \sigma \zeta_j^2 & -\tau v L \sigma \zeta_j^2 \end{pmatrix} .$$  \hspace{1cm} (D.13)
We have used the characteristic equation in the form

$$-z^2(1 + \zeta_j) - (\theta - 1)\zeta_j^2 = \zeta_j^2(1 + \zeta_j)$$

(D.14)

to obtain Eq. (4.31).
APPENDIX E: DETAILED RESULTS OF INTENSITY CALCULATIONS

In this appendix are collected the \( z \)- and \( t \)-expansions of the cross sections \( R_0 \), \( R_1 \), and \( R_B = ReP_+ \), and the quantity \( I_B = ImP_+ \) which causes the skewing of the Brillouin peaks. For convenience, we rewrite the definition

\[
A = \left( \frac{c_0}{v} \right)^2 (3\nu v k_B T).
\]

A. Thermal Peak

We recall that for our Eulerian model, the thermal peak is simply a constant cross section with a delta function shape factor,

\[
R_0 = A_0 [\epsilon_S C_{p,0}^\Lambda + \epsilon_\lambda T\Delta S]^2, \quad (E.1)
\]

where

\[
A_0 = 3\nu v k_B / \Lambda Q,
\]

\[
Q = C_{p,0}^\Lambda - T(\Delta S)^2.
\]

B. Chemical Reaction Peak

The \( t \)-expansion of this cross section is

\[
R_1 = \left( \frac{A}{\Delta_1} \right) \\
\times \left[ (\alpha \varepsilon_\lambda)^2 + 2\alpha \varepsilon_\lambda \epsilon_p t/s + \epsilon_p (4\lambda \varepsilon_\lambda z^2 + s \epsilon_p) t^2/s^3 + \ldots \right], \quad (E.2)
\]

\[
\Delta_1 = t + t^2 (1 - z^2)/s^2 + \ldots.
\]
From the $z$-expansion, we get the expression

$$R_1^{(0)} = \left( A/\Delta_1^{(0)} \right) \times \left[ (a\epsilon_\lambda + t\epsilon_p)^2 - 2z^2 \epsilon_p (a\epsilon_\lambda + t\epsilon_p)t/\theta^2 + \ldots \right] , \quad (E.3)$$

$$\Delta_1^{(0)} = \theta t - 3z^2 t^2/\theta^2 + \ldots .$$

If we use Eq. (A.33) with the assumption $\xi_T = 0$, we have the simple identity,

$$a\epsilon_\lambda + t\epsilon_p = a\epsilon_\lambda \epsilon_p , \quad (E.4)$$

which appears in $R_1^{(0)}$.

C. Brillouin Peaks

Both Brillouin peaks have the same cross section, $R_B$. The $t$-expansion for this cross section is

$$R_B = \frac{1}{2} (A/\Delta_B) [H + tH_1/s^2 + \ldots] , \quad (E.5)$$

$$H = \epsilon_p^2 - 2a\epsilon_\lambda \epsilon_p/s + a^2 \epsilon_\lambda^2 (1 - z^2)/s^2 ,$$

$$H_1 = \epsilon_p^2 (1 - 4z^2) - 2a\epsilon_\lambda \epsilon_p (1 - z^2) + (a\epsilon_\lambda)^2 ,$$

$$\Delta_B = 1 + 2t(1 - 2z^2)/s^2 + \ldots ,$$

while the $z$-expansion gives
\[ R_B^{(o)} = \frac{1}{2} (A/\Delta_B^{(o)}) \left[ \left( \varepsilon_p - \alpha \varepsilon_\lambda \right)^2 + z^2 H_1^{(o)} / \theta^3 \right] + \ldots \], \quad (E.6) \\

\[ H_1^{(o)} \approx 2\varepsilon_p^2 - 2\alpha \varepsilon_\lambda \varepsilon_p - (\alpha \varepsilon_\lambda)^2, \]

\[ \Delta_B^{(o)} \approx \theta + 2z^2 (1 - t) / \theta^2 + \ldots . \]

We have ignored terms of order \( t^2 \) in the expressions for \( H_1^{(o)} \) and \( \Delta_B^{(o)} \).

Again, Eq. (A.33) may be used with the assumption \( \bar{\varepsilon}_T = 0 \) to give

\[ \varepsilon_p - \alpha \varepsilon_\lambda = c_o^{-2} \bar{\varepsilon}_T - \bar{\varepsilon}_\lambda . \]

(E.7)

In order to completely construct the structure factors \( S_\pm \), we need the imaginary part of \( P_\pm \) as well as the real part. Since \( P_-^* = P_+ \), we designate \( I_+ = \text{Im} P_+ \) by \( I_B \) and note that \( I_- \) would just be \( -I_B \). The \( t \)-expansion of \( P_+ \) yields

\[ I_B = (A/\Delta_B)^{(2/s)} \]

\[ \times \left[ \alpha \varepsilon_\lambda \left( \varepsilon_p - \alpha \varepsilon_\lambda / s \right) + \frac{1}{2} t N_1 / s + \ldots \right], \quad (E.8) \]

\[ N_1 = (3 + z^2)\varepsilon_p^2 - 4\alpha \varepsilon_\lambda \varepsilon_p + (\alpha \varepsilon_\lambda)^2. \]

Extracting the imaginary part of the \( z \)-expansion of \( P_+ \) gives

\[ I_B^{(o)} = \frac{1}{2} (A/\Delta_B^{(o)}) \theta^{3/2} z [3t\varepsilon_p^2 + 2(2 - t)\alpha \varepsilon_\lambda \varepsilon_p - (4 + t)\alpha^2 \varepsilon_\lambda^2] + \ldots \].

(E.9)
REFERENCES


11. The notation and equations used here follow the presentation given in reference 2. The reader is referred to the appendices of that reference for background material, and Appendix A of this article.


16. This point was developed in reference 2, Sec. VII. D.


1. The z dependence of the chemical reaction peak half-width is characterized here by the function \( h(z) \), in terms of which \( \tau \Delta \omega_1(z) = 1 + \theta h(z) \). The different curves result from the various expressions for \( \Delta \omega_1 \): the \( t \)-expansion (---), the \( z \)-expansion (--), the \( 1/z \)-expansion (----). The vertical lines labelled (o) and (\( \infty \)) indicate the values of \( \ell n z_0 \) and \( \ell n z_\infty \), respectively. These are the points at which the \( z \)- and \( 1/z \)-expansions cease to adequately represent the \( t \)-expansion.

2. The \( z \) dependence of the chemical reaction peak cross-section is shown in this graph of \( R_1 \), which is scaled in units of its asymptotic value, \( R_1(\infty) \). The \( t \)-expansion in Eq. (E.2) has been used with \( t = 10^{-2} \). The dimensionless number \( b \) is \( \alpha \epsilon_\lambda / \epsilon_p \).

3. The function \( g(z) \) illustrates the \( z \) dependence of the Brillouin peak half-width according to the relationship \( \tau \Delta \omega_B(z) = \frac{1}{2} t g(z) \). The two curves show the results of the \( t \)-expansion (---) and the \( z \)-expansion (--).

4. This graph shows the dispersion of the sound speed as calculated from the displacement of the Brillouin peak. The \( t \)-expansion has been used with \( t = 10^{-3} \), and \( V(z) \) has been scaled in units of its high frequency asymptotic value \( c_0 \). The horizontal bar indicates the region of strongest dispersion.
5. The effects of the skewing factor $\xi$ are evident in this illustration of the Brillouin structure factor (scaled in units of its maximum). The abscissa $\omega$ increases toward the right. Both curves were calculated from the $t$-expansion of $S_B$ with $t = 10^{-3}$, $b = 10$, and $z = 10^2$. For this choice of parameters, $\xi = 0.20$. Neglect of the skew term gives the pure Lorentzian (dashed line) centered around $\omega_B = \beta$, while inclusion of this term results in the skewed peak (solid line). The frequencies $\omega_m$ and $\omega_p$ are the values of $\omega$ at which the intensity has fallen to half maximum.

6. The skewing factor $\xi$ is shown as a function of $z$. The curves were calculated from Eq. (8.46) with $t = 10^{-3}$. The curve for the smaller value of $b$ has been expanded ten-fold for the sake of clarity. Note that both maxima occur near $z = 1$. 
Figure 2

The graph depicts the relationship between $\ln Z$ and $(R/X) / (Z^1/R)$. Two curves are shown, one for $b=1$ and another for $b=-1$. The x-axis ranges from 0.97 to 1.02, and the y-axis ranges from 0 to 2.0.
PART II

ELECTRON SCATTERING FROM ATOMIC HYDROGEN
CHAPTER ONE
CHAPTER ONE. INTRODUCTION TO QUANTUM MECHANICS OF PARTICLE SCATTERING

This Chapter purports to be an overview of the particular scattering theory background required for the understanding by "outsiders" of the material in Chapters Two and Three of this volume. It is certainly not an integral part of the material there.

The approach taken here is admittedly pedestrian, but with a purpose. In large part, the scattering theory presented in available sources is unnecessary for understanding the present work. This chapter collects only those concepts, techniques, and equations which lead in a straightforward manner from the free particle Hamiltonian and its plane wave solutions to coupled radial equations for multi-channel scattering and the methods for obtaining cross sections from their solutions.

Most of the material used in this chapter was taken from the five references at the end of the chapter.\textsuperscript{1-5} It is divided into three major sections. The first deals with the mutual scattering of two simple (structureless) particles. The second considers the additional complexities which are involved when one of the "particles" has internal structure, while the third gives specific attention to the scattering of an electron by a hydrogen atom and the formulation in terms of a coupled angular and spin momenta basis set.
1. SIMPLE ELASTIC SCATTERING

The Scattering Process

Consider two masses, \( m_1 \) and \( m_2 \), situated at \( r_1 \) and \( r_2 \), which interact through a central potential \( V(r) \), \( r = |r_1 - r_2| \). Choose the energy scale such that the state of zero energy has both particles at rest at infinite separation. Then require further that

\[
\lim_{r \to \infty} r V(r) = 0. \tag{1.1}
\]

In discussing actual problems, the potential will be assumed to satisfy

\[
V(r) \approx 0, \quad r > \bar{R}, \tag{1.2}
\]

where \( \bar{R} \) is the effective "range" of \( V(r) \).

Removal of the uniform center of mass motion and its associated translational energy gives the following expression for the Schrödinger equation,

\[
\left[ (-\hbar^2/2\mu) \frac{\partial^2}{\partial r^2} + V(r) - E \right] \psi_R(r) = 0, \tag{1.3}
\]

where \( \mu \) is the reduced mass, \( m_1 m_2/(m_1 + m_2) \), and the kinetic energy operator is with respect to the relative coordinate (subscript \( r \)).

The practical study of scattering may then be described as the study of the positive energy solutions of Eq. (1.3). Several quite general properties of such solutions are

1) they exist for any \( E \);
2) they are oscillatory;
3) they are finite throughout space.

The implication of property 3) is that there is a finite probability density even at infinite separation of the particles.

Now consider an elastic scattering experiment with the following description:

1) a projectile is shot at a target from a source much further away than \( \bar{R} \), with specified energy \( E \) and momentum \( \hbar k_0 \);

2) the projectile first propagates as a free particle (free wave), then interacts with the target (altering its shape), and finally moves away as a free particle again (free wave, but with altered phase);

3) the scattered projectile is detected, again at a distance greater than \( \bar{R} \) away from the target, with the same energy \( E \), but with momentum \( \hbar k \), where \( |k| = |k_0| \) but the direction has changed.

Note the more or less one-to-one correspondence between the experiment description and the general properties of \( \psi_E(r) \). Intuitively then, one may feel that such wavefunctions can actually provide the description of a scattering process. How such correspondence is actually made will be seen later.

**Free Waves**

Since the function describing the scattering is to be viewed as a modified free wave, it is logical to begin with a short discussion of
true free waves. The Hamiltonian for these is just

\[ H = \frac{p^2}{2\mu} = \left( -\frac{\hbar^2}{2\mu} \right) \nabla^2, \quad (1.4) \]

so that the Schrödinger equation for energy \( E \) may be written

\[ (\nabla^2 + k^2) \phi_k(r) = 0. \quad (1.5) \]

Here, \( k \) is a wave vector whose magnitude is

\[ k = (k \cdot k)^{\frac{1}{2}} = (2\mu E / \hbar^2)^{\frac{1}{2}} \quad (1.6) \]

and whose direction is the direction of propagation. This can be seen by solving Eq. (1.5) in Cartesian coordinates, which yields the unnormalized eigenfunctions

\[ \phi_k^p(r) = c(k) e^{i k \cdot r}. \quad (1.7) \]

These functions are called plane waves (superscript \( p \)), since all points of given phase lie on a plane perpendicular to \( k \). Although the magnitude of \( k \) is fixed, its direction is completely arbitrary; hence for a given \( E \), there is an infinite set of eigenfunctions \( \phi_k^p(r) \). Using Eq. (1.7) in the quantum mechanical flux density expression gives

\[ j = \frac{\hbar}{2\mu i} [\phi^* \nabla \phi - (\nabla \phi)^* \phi] = (\hbar k / \mu) |c(k)|^2 = v |c(k)|^2, \quad (1.8) \]

where \( v \) is the velocity corresponding to the momentum \( \hbar k \). Usually, all \( c(k) \) are set equal to unity, and the resulting eigenfunctions are said to be normalized to unit flux in the direction \( k \).
The set of all \( \phi_k^p(r) \) is complete with respect to the positive \( E \) solutions of Eq. (1.5); i.e., any function \( \phi(r) \) written as

\[
\phi(r) = \int g(k) \phi_k^p(r) \, d\Omega_k
\]

is a solution of Eq. (1.5) with energy \( E \). The integral is over all directions of \( k \), since its magnitude is fixed.

There is another set of solutions of Eq. (1.5) which is equally as important for scattering as the \( \phi_k^p(r) \). These are the spherical waves, which may be introduced as follows. If Eq. (1.5) is written in spherical polar coordinates, it reads

\[
\left[ \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \lambda^2 r^2 + k^2 \right] \phi_k^s(r, \hat{r}) = 0,
\]

where \( \hat{\lambda} \) is the angular momentum operator in units of \( \hbar \), and the eigenfunction has been superscripted with "s" to indicate its dependence on the spherical coordinates. These coordinates are denoted by \( (r, \hat{r}) \), where \( r = |r| \), and \( \hat{r} \) is the unit vector in the direction of \( r \), \( \hat{r} = r/r \).

Using the angular momentum eigenfunctions (spherical harmonics), for which

\[
\hat{\lambda}^2 Y_{\lambda m}(\hat{r}) = \lambda(\lambda + 1) Y_{\lambda m}(\hat{r}),
\]

it is possible to express various solutions of Eq. (1.10) as

\[
\phi_{k, \lambda, m}^s(r, \hat{r}) = r^{-\lambda} y_{k, \lambda}(r) Y_{\lambda m}(\hat{r}),
\]

where the radial functions \( y \) must satisfy the equation

\[
\left[ \frac{d^2}{dr^2} + k^2 - \frac{\lambda(\lambda + 1)}{r^2} \right] y_{k, \lambda}(r) = 0.
\]
The solutions of this equation are the Ricatti-Bessel functions. The solution which is regular at the origin is

\[ y_{\ell, k}(r) = F_{\ell}(kr) = kr j_{\ell}(kr), \]  

(1.14)

and the irregular solution is

\[ y_{\ell, k}(r) = G_{\ell}(kr) = kr n_{\ell}(kr), \]  

(1.15)

where \( j_{\ell}(\rho) \) and \( n_{\ell}(\rho) \) denote the spherical Bessel and Neumann functions, respectively. Asymptotically, these functions have very simple behavior: for \( kr >> \frac{1}{2} \ell(\ell + 1) \),

\[ F_{\ell}(kr) \sim \sin (kr - \ell\pi/2), \]  

(1.16)

\[ G_{\ell}(kr) \sim \cos (kr - \ell\pi/2). \]  

(1.17)

Alternative irregular solutions result from various choices of \( \gamma \) in the expression

\[ G_{\ell}(kr) + \gamma F_{\ell}(kr). \]

The Hankel functions of the first and second kind arise from the choices \( \gamma = \pm i \),

\[ H_{\ell}^{(+)}(kr) = G_{\ell}(kr) + i F_{\ell}(kr), \]  

(1.18a)

\[ H_{\ell}^{(-)}(kr) = G_{\ell}(kr) - i F_{\ell}(kr). \]  

(1.18b)

Using Eqs. (1.16) and (1.17), these functions are seen to have the asymptotic behavior of outgoing and incoming spherical waves,
\[ H^\pm (kr) \sim e^{i(kr - \frac{\pi}{2})}. \]  

(1.19)

The terminology comes from a calculation of the flux associated with

\[ \phi_{k, \ell, m}^s (r, \hat{r}) = C_{\ell, k} r^{-1} H^\pm (kr) Y_{\ell m} (\theta, \phi), \]

which is

\[ \sim \pm \left( \frac{\hbar k}{ur^2} \right) |C_{\ell, k}|^2 \hat{r} + o(r^{-3}) \]  

(1.20)

and thus becomes purely radial for large \( r \). Note that this flux is constant over the area of a sphere as \( r \to \infty \).

To describe a free wave in space, including the origin, only the regular solutions are appropriate, and ignoring normalization,

\[ \phi_{k, \ell, m}^s (r, \hat{r}) = j^\pm (kr) Y_{\ell m} (\theta, \phi). \]  

(1.21)

Corresponding to Eq. (1.9) is the expression

\[ \phi (r) = \sum_{\ell = 0}^{\infty} \sum_{m = -\ell}^{\ell} g_{\ell, m} j^\pm (kr) Y_{\ell m} (\theta, \phi). \]  

(1.22)

Now, since the plane waves \( \phi_k^p \) and the spherical waves \( \phi_{k, \ell, m}^s \) both form complete sets of solutions for Eq. (1.5), it must be possible to express one set in terms of the other. Indeed, if \( \phi \) in Eq. (1.22) is \( e^{ik \cdot r} \), one gets the relationship, known as the Bauer formula,

\[ e^{ik \cdot r} = \sum_{\ell = 0}^{\infty} (2\ell + 1) i^\ell j^\pm (kr) P_\ell (\cos \theta), \]  

(1.23a)

\[ = 4\pi \sum_{\ell = 0}^{\infty} \sum_{m} i^\ell j^\pm (kr) Y_{\ell m}^* (\hat{k}) Y_{\ell m} (\hat{r}), \]  

(1.23b)
where \( \hat{\mathbf{k}} \) and \( \hat{\mathbf{r}} \) are unit vectors with \( \hat{\mathbf{k}} \cdot \hat{\mathbf{r}} = \cos \theta \). Equation (1.23b) results from using the addition theorem for spherical harmonics.

Scattered Waves and Cross Sections

It is now the task to see how \( V(r) \) alters the free wave behavior. An essential feature of scattering theory is that scattering information (of the laboratory variety) is derived from the asymptotic behavior of the wavefunction for the system. Thus, most of our attention will focus on the properties which the wavefunction must show in the asymptotic region, while acknowledging that this function is actually determined by \( V(r) \) and can be practically constructed in the interaction region only by a numerical integration.

The Schrödinger equation may be written as

\[
(\nabla^2 + k^2) \psi_E(r) = U(r)\psi_E(r)
\]  

(1.24)

where \( U(r) = (2\mu/\hbar^2)V(r) \). This shows how the potential is a perturbation on free wave behavior. The most general solution of this equation is of the form

\[
\psi_E(r) = \phi(r) + \psi_S(r),
\]

(1.25)

that is, a solution of the homogeneous equation, Eq. (1.5), plus a particular solution of Eq. (1.24). These will be chosen in such a way that the asymptotic form of \( \psi_E \) satisfies boundary conditions appropriate to the scattering problem. The plane wave solutions of Eq. (5) will be
chosen for \( \psi(r) \) since they represent flux along a wave vector \( k \) which can be pointed at the target to represent the incident projectile.

Evidently, \( \psi_s(r) \) must represent the scattered wave. Such solutions are best obtained by use of the Green functions which are discussed later. That technique can be used to show that, \textit{asymptotically}, \( \psi_s \) looks like an angle-dependent factor multiplying the asymptotic form of one of the irregular spherical waves. The angle is related to the two directions involved in defining the problem. These are \( k_0 \), the direction of incidence, and \( k \), the direction of scattering. It is true that scattering occurs in every direction \( k \), since only \( |k| \) is fixed by energy conservation, but we are thinking of a detector placed at one particular direction from the target and we want the asymptotic value of \( \psi_E(r) \) at that point. Thus, the angle is the one between \( \tilde{k}(=\tilde{\xi}) \) pointing at the detector, and \( k_0 \).

The asymptotic form of \( \psi_s(r) \) is then written

\[
\psi_s(r) \sim f_0(\tilde{\xi}) \frac{e^{ikr}}{r}.
\]  

(1.26)

The angular factor, \( f_0(\tilde{\xi}) \), has been subscripted to denote its dependence on the incident wave vector \( k_0 \), and the irregular spherical wave chosen is the one having purely radial outgoing flux in the asymptotic region, in accord with our intuitive feelings about \( \psi_s \). The full solution of the scattering equation is thus expected to have the asymptotic behavior

\[
\psi(k_0|\tilde{r}) \sim e^{-i\cdot\tilde{r}} + f_0(\tilde{\xi}) \frac{e^{ikr}}{r},
\]

(1.27)

where the explicit dependence of \( \psi \) on \( k_0 \) has been shown. Since \( f_0(\tilde{\xi}) \) modulates the amount of scattering in each direction, it is called the scattering amplitude.
It is this coefficient \( f_o(\hat{r}) \) which carries the scattering information out of the interaction region into the asymptotic region where it manifests its existence in the scattering cross section. The exact relationship between \( f_o \) and the differential cross section \( d\sigma_o(\hat{r})/d\Omega \) can be found by constructing a wave packet out of the stationary state solutions \( \psi(k_o | r) \) and following its development in time. (It is such a calculation that actually verifies that the assumed asymptotic form in Eq. (1.27) is the correct one.) The results obtained in this correct manner turn out to be equivalent to simply analyzing Eq. (1.27) in terms of the fluxes associated with each term. Using the expressions in Eqs. (8) and (20), it is seen that \( \psi(k_o | r) \) represents an incident flux along \( k_o \) of

\[
|j(\text{incident})| = \left( \frac{\hbar k_o}{\mu} \right),
\]

and an outgoing radial flux

\[
|j(\text{scattered})| = \left( \frac{\hbar k}{\mu} \right) \frac{|f_o(\hat{r})|^2}{r^2}.
\]

The flux received into a detector of face area \( dA = r^2 d\Omega \) is

\[
|j(\text{detected})| d\Omega = \left( \frac{\hbar k}{\mu} \right) |f_o(\hat{r})|^2 d\Omega.
\]

The differential cross section for scattering in the direction \( k \) is just the ratio of detected flux per unit solid angle to incident flux, and using Eqs. (1.28) and (1.30), this is

\[
\frac{d\sigma_o(\hat{r})}{d\Omega} = \frac{k}{k_o} |f_o(\hat{r})|^2 = |f_o(\hat{r})|^2,
\]

the second equality following since \( k_o \) and \( k \) have the same magnitude.
Partial Wave Analysis

A very useful and important technique in practical scattering theory, the method of partial waves, will now be introduced. The basic idea is simply that the function space to which the solutions of Eq. (1.24) belong is the same as that to which the solutions of Eq. (1.5) belong. Thus, functions of the form

\[
\phi_{k, \ell}(r, \theta) = \left(\frac{4}{2\pi+1}\right)^{1/2} r^{-1} y_{k, \ell}(r) Y_{\ell \theta}(\hat{r}) \\
= r^{-1} y_{k, \ell}(r) P_{\ell}(\cos \theta)
\]  

(1.32)

can be used as a basis for expanding \( \psi(\mathbf{k}_0 | r) \). Note that the azimuthal angle is irrelevant here since the spherical symmetry of \( V(r) \) implies cylindrical symmetry about \( \mathbf{k}_0 \), and the z-axis has been taken along \( \mathbf{k}_0 \). The partial wave expansion is stated as

\[
\psi(\mathbf{k}_0 | r) = \sum_{\ell=0}^{\infty} r^{-1} y_{k, \ell}(r) P_{\ell}(\cos \theta),
\]

(1.33)

and this will solve Eq. (1.24) if the \( y_{k, \ell} \) satisfy equations similar to Eq. (1.13), namely

\[
\left[ \frac{d^2}{dr^2} + \frac{k^2 + \ell(\ell+1)}{r^2} - U(r) \right] y_{k, \ell}(r) = 0, \quad r < \bar{R}.
\]

(1.34)

Thus, the solution of the partial differential equation in three variables has been reduced to solving a set of ordinary differential equations, but at the expense of an infinite number of solutions to be found and summed over.
In order to complete the partial wave analysis, it is necessary to see how the asymptotic form of \( \psi \) is related to the \( y_{\ell,k} \), and in particular, how the scattering amplitude is to be calculated.

The asymptotic form of \( y_{\ell,k}(r) \) is found as follows. If \( U(r) \) were zero, recall that these radial functions would just be the regular solutions \( F_{\ell}(kr) \). The presence of \( U(r) \), however, will tend to introduce a certain amount of irregular behavior component into \( y_{\ell,k}(r) \) as \( r \) moves out from the origin. Thus, beyond the range of the potential, it should be possible to represent \( y_{\ell,k} \) by

\[
y_{\ell,k}(r) = N_{\ell}^{(1)} \left[ F_{\ell}(kr) + R_{\ell} G_{\ell}(kr) \right], \quad r > \bar{R}
\]  

which goes asymptotically as

\[
y_{\ell,k}(r) \sim N_{\ell}^{(1)} \left[ \sin(kr - \ell \pi/2) + R_{\ell} \cos(kr - \ell \pi/2) \right].
\]  

The constant \( N_{\ell}^{(1)} \) is an overall normalization constant, while \( R_{\ell} \) is apparently the measure of scattering. Both constants depend implicitly on the scattering energy. It is expected that \( f_0 \) will depend on the set of coefficients \( \{R_{\ell}\} \). To find the relationship, the "physical" asymptotic form, Eq. (1.27), is expanded in "partial waves" by using the Bauer expansion, Eq. (1.23a). The result is

\[
r \psi(k_0 | r) \sim \sum_{\ell=0}^{\infty} (2\ell + 1) i^{\ell} r_{\ell}(kr) P_{\ell}(\cos \theta) + f_0(\theta) e^{ikr}
\]

\[
\sim \left[ f_0(\theta) + \sum_{\ell} \frac{2\ell+1}{21k} P_{\ell}(\cos \theta) \right] e^{ikr}
\]

\[
+ \left[ \sum_{\ell} \frac{2\ell+1}{21k} (-)^{\ell+1} P_{\ell}(\cos \theta) \right] e^{-ikr},
\]  

(1.37)
where the asymptotic form of \( F_\ell (kr)/k = r j_\ell (kr) \) was used to obtain the second line. If Eq. (1.36) is substituted into Eq. (1.31) and similar manipulations made, the result is

\[
 r \psi (k_0 r) \sim \left[ \sum_\ell \frac{N_\ell^{(1)}}{2i} (-1)^\ell (1 + i R_\ell) P_\ell (\cos \theta) \right] e^{ikr} \\
+ \left[ \sum_\ell \frac{N_\ell^{(1)}}{2i} i^\ell (-1 + i R_\ell) P_\ell (\cos \theta) \right] e^{-ikr} . \tag{1.38}
\]

Comparing the coefficients of \( e^{-ikr} \) in Eqs. (1.37) and (1.38), and writing a term by term equality due to the orthogonality of the \( P_\ell \)'s, the normalization constants are found to be

\[
 N_\ell^{(1)} = \frac{2\ell + 1}{k} \frac{i^\ell}{1 - i R_\ell} . \tag{1.39}
\]

Comparing likewise the coefficients of the outgoing waves gives

\[
 f_0 (\theta) = \sum_\ell \frac{N_\ell^{(1)}}{2i} (-1)^\ell (1 + i R_\ell) \left( \frac{2\ell + 1}{2ik} \right) P_\ell (\cos \theta) , \tag{1.40}
\]

and using Eq. (1.39) for \( N_\ell^{(1)} \),

\[
 f_0 (\theta) = k^{-1} \sum_\ell (2\ell + 1) \left( R_\ell^2 / (1 - i R_\ell) \right) P_\ell (\cos \theta) . \tag{1.41}
\]

This result accomplishes the goal of expressing the scattering amplitude in terms of quantities characteristic of the asymptotic form of the solutions of the radial equations.

To make connection with the more usual treatment of elastic scattering from spherical potentials, note that a real phase angle \( \delta_\ell \) may be defined by

\[
 \tan \delta_\ell = R_\ell . \tag{1.42}
\]
The asymptotic form of Eq. (1.36) then reads

\[ y_{\ell,k}(r) \sim \left[ N_{\ell}^{(1)} / \cos \delta_{\ell} \right] \sin(kr - \ell \pi/2 + \delta_{\ell}), \]  

and it is evident that the influence of the potential is to shift the phase of the scattered wave relative to a free wave. Further trigonometry also shows that

\[ [R_{\ell}/(1 - iR_{\ell})] = e^{i\delta_{\ell}} \sin \delta_{\ell}, \]  

which is the expression normally encountered in the brackets in Eq. (1.41).

The problem of computing the scattering amplitude has been reduced to finding either the set of coefficients \( \{ R_{\ell} \} \), or the set of phase shifts \( \{ \delta_{\ell} \} \). This may be accomplished by simply integrating (numerically) Eq. (1.34) out from the origin to some point \( r_0 \gg R \). For the initial conditions, one uses

\[ y_{\ell,k}(0) = 0, \quad y_{\ell,k}'(0) = \left[ \frac{d}{dr} y_{\ell,k}(r) \right]_{r=0} = \gamma_{\ell,k}, \]  

where \( \gamma_{\ell,k} \) is a real constant which only affects the normalization of \( y_{\ell,k}(r) \). At \( r_0 \), the numerical function may be matched to the required asymptotic form, Eq. (1.36) for example. The requirement of continuity of the logarithmic derivative at \( r_0 \) is expressed in the equation

\[ y_{\ell,k}'(r_0)/y_{\ell,k}(r_0) = [F'(k r_0) + R_{\ell} G_{\ell}'(k r_0)]/[F_{\ell}(k r_0) + R_{\ell} G_{\ell}(k r_0)], \]  

which may be simply solved for \( R_{\ell} \) in terms of the numerical values of the other functions. Note that \( N_{\ell}^{(1)} \) is unimportant here.

According to Eq. (1.33), this procedure is to be repeated for all \( \ell \) values from zero to infinity. Fortunately, this is not necessary in
practice, and often only the first few partial waves need be computed. This fairly rapid convergence of the series in Eq. (1.41) can be argued with the following semi-classical considerations. In the partial wave expansion, each term \( \phi_{k,\ell} \) is an angular momentum eigenfunction

\[
\hat{\ell}^2 \phi_{k,\ell} = \ell(\ell + 1) \phi_{k,\ell}. \tag{1.47}
\]

Classically, for a fixed incident velocity, \( v_0 = h k_0 / \mu \), each value of the angular momentum around the origin corresponds to an impact parameter

\[
b_\ell \leftrightarrow \frac{\sqrt{\ell(\ell + 1)h^2}}{\mu v_0} \approx \frac{\ell}{k_0}. \tag{1.48}
\]

Thus an impact parameter can be associated with each radial function \( y_{\ell,k} \).

Consider first the scattering of relatively slow particles. For larger values of \( \ell \) (i.e. higher terms in the partial wave expansion), \( b_\ell \) is large enough that only the relatively weak outer portion of \( V(r) \) is being seen by the wave, and each successive term in the series will be less and less influenced (more free wave-like, \( R_\ell \to 0 \)). This is just a manifestation of the centrifugal potential barrier which appears in Eq. (1.34). One concludes that most low energy scattering appears in the small \( \ell \) terms and only these \( R_\ell \) need to be calculated.

On the other hand, this does not mean that the partial wave expansion is of little utility for high energy scattering. Further on, expressions for \( R_\ell \) will be derived which are integrals over \( V(r) \) times \( y_{\ell,k}(r) \). At high energies, the effects of \( V(r) \) should not be very great, and \( y_{\ell,k} \) should be nearly a free wave for all \( \ell \). This approximation (called the Born approximation) can be used in the integrals to estimate the magnitudes of the \( R_\ell \) very simply. Thus, the equations for \( y_{\ell,k}(r) \) need not
be integrated, and there is no problem in using even a hundred terms
if necessary in Eq. (1.41).

In order to understand later work, it is convenient here to intro-
duce alternate asymptotic forms for \( y_{l,k} \). Though not practical com-
putationally (since they are complex), they will nevertheless prove to be
useful in the formulation of multichannel scattering. The only difference
between the various forms is the choice of which two linearly independent
spherical wave functions are to be used to characterize \( y_{l,k} \) in the
asymptotic region. The practical implication of the various choices is
to change the initial derivative condition, \( c_{l,k} \), since \( y_{l,k}(0) = 0 \) always.

Consider first representing \( y_{l,k}(r) \) outside the range of the potential
by \( F_{l}(kr) \) and \( H_{l}^{(+)}(kr) \):

\[
y_{l,k}(r) = N_{l}^{(2)} [F_{l}(kr) + T_{l} H_{l}^{(+)}(kr)], \quad r > R,
\]

\[
\sim N_{l}^{(2)} [\sin(kr - \ell \pi/2) + T_{l} \exp i(kr - \ell \pi/2)] \quad (1.49)
\]

The scattering information is now contained in a new set of coefficients
\( \{T_{l}\} \). By using the relation \( e^{iz} = \cos z + i \sin z \), it can be seen that
the relationship between this and the previous asymptotic expression for
\( y_{l,k}(r) \) is

\[
R_{l} = T_{l}/(1 + iT_{l}) \quad (1.50a)
\]

\[
N_{l}^{(1)} = N_{l}^{(2)} (1 + iT_{l}) \quad (1.50b)
\]

Inverting these gives

\[
T_{l} = R_{l}/(1 - iR_{l}) \quad (1.51a)
\]

\[
N_{l}^{(2)} = N_{l}^{(2)} \frac{2l + 1}{k} \quad (1.51b)
\]
The first of these shows that from the current viewpoint, the scattering amplitude is given by

\[ f_o(\theta) = -\sum_{\ell} (2\ell + 1) T_{\ell} P_{\ell}(\cos \theta). \quad (1.52) \]

Another alternative is to choose the linearly independent solutions \( H_{\ell}^{(-)} \) and \( H_{\ell}^{(+)} \):

\[ y_{\ell,k}(r) = N_{\ell}^{(3)} [H_{\ell}^{(-)}(kr) - S_{\ell} H_{\ell}^{(+)}(kr)], \quad r > R \]

\[ \sim N_{\ell}^{(3)} [\exp -i(kr - \ell \pi/2) - S_{\ell} \exp i(kr - \ell \pi/2)]. \quad (1.53) \]

For this case, the following correspondences may be made,

\[ R_{\ell} = i(1 - S_{\ell})/(1 + S_{\ell}), \quad (1.54a) \]

\[ T_{\ell} = \frac{1}{2} (1 - S_{\ell}), \quad (1.54b) \]

\[ N_{\ell}^{(3)} = -\frac{2\ell + 1}{2ik} \ell. \quad (1.54c) \]

There are thus a number of different ways of formulating the mathematical boundary conditions, but since they must all reproduce the "physical" condition stated in Eq. (1.27), they must all be equivalent. Regardless of which set, \( \{R_{\ell}\}, \{T_{\ell}\}, \) or \( \{S_{\ell}\}, \) one wishes to consider basic, any of the others are easily calculated from it. The three types of coefficients which have been introduced are the one-dimensional analogs of the "reactance" matrix \( R \), "transition" matrix \( T \), and "scattering" matrix \( S \), which are used to describe multichannel scattering.
Green Functions and Scattering

So far, scattering has been discussed in the framework of the differential equations arising from the coordinate representation of the Schrödinger equation. It will now be formulated in terms of the integral equations which are equivalent to those differential relations. The formal technique for making such conversions is the Green function method. The general idea is shown in the following discussion.

Suppose a differential operator \( D(r) \) is given, along with the solutions \( \omega_0(r) \) to

\[
D(r) \omega_0(r) = 0, \quad 0 \leq r \leq \infty, \quad (1.55)
\]

and it is desired to solve the non-homogeneous problem

\[
D(r) \omega(r) = \rho(r), \quad 0 \leq r \leq \infty. \quad (1.56)
\]

This may be accomplished by combining the solutions \( \omega_0(r) \) to form a function, called a Green function, which satisfies the symbolic equation

\[
D(r) G(r,r') = \delta(r - r'). \quad (1.57)
\]

When this has been done, a particular solution of Eq. (1.56) can be expressed by

\[
p(r) = \int_0^\infty G(r,r') \rho(r') \, dr', \quad (1.58)
\]

since

\[
D(r) p(r) = \int_0^\infty [D(r) G(r,r')] \rho(r') \, dr'
= \int_0^\infty \delta(r - r') \rho(r') \, dr'' = \rho(r). \quad (1.59)
\]
The most general solution of Eq. (1.56) is then given by the expression

\[ \omega(r) = \lambda \omega_0(r) + p(r) \]  \hspace{1cm} (1.60)

where \( \lambda \) is an arbitrary constant which can be adjusted to satisfy the boundary conditions. Note that in scattering problems,

\[ \rho(r) = V(r) \omega(r), \]  \hspace{1cm} (1.61)

so one is involved with an integral equation for \( \omega(r) \),

\[ \omega(r) = \lambda \omega_0(r) + \int_0^\infty G(r, r') V(r') \omega(r') \, dr'. \]  \hspace{1cm} (1.62)

These considerations will now be applied to the radial differential equations.

For convenience, Eqs. (1.13) and 1.34) are rewritten here as

\[ \frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell + 1)}{r^2} \omega_\ell(r) = 0 \]  \hspace{1cm} (1.63)

\[ \frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell + 1)}{r^2} y_\ell(r) = U(r) y_\ell(r). \]  \hspace{1cm} (1.64)

The subscript \( k \) is conveniently omitted. Denote the regular and irregular solutions of Eq. (1.63) by \( f_\ell(r) \) and \( g_\ell(r) \), respectively. According to Eq. (1.57), these are to be combined to give a function \( G_\ell(r, r') \) satisfying

\[ \frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell + 1)}{r^2} G_\ell(r, r') = \delta(r - r'). \]  \hspace{1cm} (1.65)

If this equation is integrated from \( r = r' - \epsilon \) to \( r = r' + \epsilon \) (\( \epsilon \) small and positive), and then the limit taken as \( \epsilon \to 0 \), one obtains
\[
\lim_{\varepsilon \to 0} \frac{d}{dr} G_{\lambda}(r, r') \bigg|_{r' - \varepsilon}^{r' + \varepsilon} = 1, \tag{1.66}
\]

so \( G_{\lambda}(r, r') \) is to have a unit discontinuity in its slope at \( r = r' \).

For \( r \neq r' \), Eq. (1.65) requires that \( G_{\lambda} \) have the form

\[
G_{\lambda}(r, r') = \begin{cases} 
  f_{\lambda}(r) \ u_{\lambda}(r'), & r < r', \\
  g_{\lambda}(r) \ v_{\lambda}(r'), & r > r', 
\end{cases} \tag{1.67}
\]

since its \( r \)-dependence must satisfy Eq. (1.63). The functions \( u_{\lambda} \) and \( v_{\lambda} \) are as yet undetermined.

Next, suppose an equation of the form of Eq. (1.65) is written with the singularity at \( r'' \), and \( G_{\lambda}(r, r') \) times that equation is subtracted from \( G_{\lambda}(r, r'') \) times Eq. (1.65). The result,

\[
G_{\lambda}(r, r'') \frac{d^2 G_{\lambda}(r, r')}{dr^2} - G_{\lambda}(r, r') \frac{d^2 G_{\lambda}(r, r'')}{dr^2} = \delta(r - r') \ G_{\lambda}(r, r'') - \delta(r - r'') \ G_{\lambda}(r, r'), \tag{1.68}
\]

may be integrated from \( r_1 < (r', r'') \) to \( r_2 > (r', r'') \) to get

\[
[G_{\lambda}(r, r') \ G'_{\lambda}(r, r'') - G_{\lambda}(r, r'') \ G'_{\lambda}(r, r')]_{r = r_1}^{r = r_2} = G_{\lambda}(r', r'') - G_{\lambda}(r'', r'). \tag{1.69}
\]

By employing Eq. (1.67), it can be shown that the expression in brackets vanishes at both \( r_1 \) and \( r_2 \), hence \( G_{\lambda} \) must be a symmetric function of its arguments,

\[
G_{\lambda}(r', r'') = G_{\lambda}(r'', r'). \tag{1.70}
\]
One immediately sees that

\[ u_\lambda'(r') = C \, g_\lambda(r'), \quad (1.71a) \]

\[ v_\lambda'(r') = C \, f_\lambda(r'). \quad (1.71b) \]

The constant of proportionality can be determined from Eq. (1.66).

Using Eqs. (1.71) and (1.67) in (1.66) gives \(-C W_\lambda = 1\), or

\[ C = -W^{-1}_\lambda \]

\[ = -[f_\lambda' \, g_\lambda - g_\lambda' \, f_\lambda]^{-1} \quad (1.72) \]

where \( W_\lambda \) is the Wronskian of \( f_\lambda \) and \( g_\lambda \), and turns out to be independent of \( r \) for differential equations of the form of Eqs. (1.63) or (1.64) (Wronskian Theorem). From Eq. (1.72) it is now evident why \( G_\lambda \) must look like one of the irregular solutions \( g_\lambda \) in its larger argument; otherwise the unit discontinuity in \( G_\lambda' \) would not exist since \( W_\lambda \) would be zero.

Notice that \( G_\lambda \) is independent of the normalization of either \( f_\lambda \) or \( g_\lambda \).

In summary, the radial functions satisfy the integral equation

\[ y_\lambda(r) = f_\lambda(r) - W^{-1}_\lambda \int_0^\infty f_\lambda'(r') \, g_\lambda(r') \, U(r') \, y_\lambda(r') \, dr' \quad (1.73) \]

where \( r_<(r_>) \) is the lesser (greater) of the two arguments \( r \) and \( r' \).

From this equation it can be seen that \( y_\lambda(r) \) does have the expected asymptotic form,

\[ y_\lambda(r) \sim f_\lambda(r) - g_\lambda(r) \, W^{-1}_\lambda \int_0^\infty f_\lambda'(r') \, U(r') \, y_\lambda(r') \, dr' \quad (1.74) \]

In this expression, \( r \) has been assumed to be larger than \( R \) so the integral limit can be extended to infinity. This equation may be used to deduce
expressions for the various scattering coefficients. For a general formulation, take

\begin{align}
  f_\ell(r) &= F_\ell(kr), \\
  g_\ell(r) &= G_\ell(kr) + \gamma F_\ell(kr),
\end{align}

(1.75a) (1.75b)

where \( \gamma_\ell \) is an arbitrary coefficient. For these choices, \( W_\ell = k \).

Consider the case of all \( \gamma_\ell = 0 \). Then

\[
y_{\ell, k}(r) \sim \sin(kr - \ell \pi/2)
+ \left[ -k^{-1} \int_0^\infty F_\ell(kr') U(r') y_{\ell, k}(r') dr' \right] \cos(kr - \ell \pi/2),
\]

(1.76)

and one readily makes the identification

\[
  R_\ell = -k^{-1} \int_0^\infty F_\ell(kr') U(r') y_{\ell, k}(r') dr'.
\]

(1.77)

In this equation it must be remembered that \( y_{\ell, k} \) is the solution normalized according to Eq. (1.76). Alternatively, all \( \gamma_\ell \) may be taken equal to \( i \), with the result

\[
y_{\ell, k}(r) \approx \sin(kr - \ell \pi/2) + T_\ell \exp i(\ell \pi/2),
\]

(1.78)

where

\[
  T_\ell = -k^{-1} \int_0^\infty F_\ell(kr') U(r') y_{\ell, k}(r') dr'.
\]

(1.79)

This expression is not equivalent to that in Eq. (1.77) since the \( y_{\ell, k} \) are normalized to the expression in Eq. (1.78).

The Born approximation referred to earlier may now be explicitly stated. Equation (1.74) can be seen to suggest that if \( k \) is large and/or \( U(r) \) is "small", that to a good approximation

\[
y_\ell(r) \approx f_\ell(r).
\]

(1.80)
Using this in Eq. (1.74) gives the approximate solution

$$y_k(r) = f_k(r) - \frac{1}{2\pi} \int_0^\infty f_k(r) g_k(r') U(r') f_k(r') dr'. \quad (1.81)$$

This may in turn be substituted under the integral term in Eq. (1.74) to yield a better approximation to $y_k$. Continuation of this process gives a series expression for $y_k$ in terms of powers of the potential $U(r)$. This is called the "Born series". If only the first term is retained, one has Eq. (1.81), which is called the "Born approximation". Applying this to Eq. (1.77) yields an approximate value for the $R_k$ coefficients,

$$R_k \approx -\kappa^{-1} \int_0^\infty [F_k(kr')]^2 U(r') dr'. \quad (1.82)$$

The method of Green functions has been applied to construct integral forms of the radial equations. It can be applied as well directly to Eq. (1.24) to generate an integral equation for the full wavefunction $\psi(k_0 | r')$ and obtain an integral definition of the scattering amplitude.

The Green function of interest is defined by the equation

$$(\nabla^2 + k_0^2) G(r, r') = \delta(r - r'). \quad (1.83)$$

The solution of this equation may be effected by use of the Fourier transform if $G(r, r')$ is assumed to have the form $G(r - r')$. By substituting

$$G(r - r') \equiv G(\rho) = \int g(k) e^{i k \cdot \rho} dk \quad (1.84)$$

into Eq. (1.83) and using

$$\delta(r - r') = \frac{1}{2\pi} \int e^{i k \cdot \rho} dk, \quad (1.85)$$
it is found that \( g(k) \) must be given by

\[
g(k) = \left( \frac{1}{2\pi} \right)^3 \frac{2}{(k_o^2 - k^2)}\end{equation}\]

(1.86)

Thus, the Green function is

\[
G(\rho) = \left( \frac{1}{2\pi} \right)^3 \int \frac{e^{ik \cdot \rho}}{(k_o^2 - k^2)} \, dk
\]

(1.87)

The integration over the angles of \( k \) is easily accomplished by choosing \( \rho \) as the z-axis and employing the integral

\[
\int e^{ik \cdot \rho} \, d\Omega_k = 4\pi \frac{\sin k\rho}{k\rho}
\]

(1.88)

The resulting expression for \( G \) is

\[
G(\rho) = \left( \frac{1}{2\pi} \right)^3 \frac{4\pi}{\rho} \int_0^\infty \frac{k \sin k\rho}{k_o(k_o^2 - k^2)} \, dk
\]

\[
= -\frac{1}{4\pi \rho} \int_0^\infty \frac{k \sin k\rho}{(k - k_o)(k + k_o)} \, dk.
\]

(1.89)

Notice in the second integral that the lower limit has been extended to negative infinity and the result divided by two since the integrand is an even function of \( k \). This is in preparation for doing a contour integration to evaluate \( G \).

There is a definite problem with this definition of the Green function—the integrand contains simple poles at \( k = \pm k_o \). One technique for overcoming this difficulty is to evaluate the integral as a contour integral in the complex \( k \)-plane with the poles displaced infinitesimally off the real axis, and then take the limit as the displacement goes to zero. If the pole at \( k_o \) is displaced by \( \imath \epsilon \) and that at \(-k_o \) by \(-\imath \epsilon \), and the contour closed by a semicircle at infinity, the result is
\[ G(\rho) = -\frac{e^{ik_o \cdot \rho}}{4\pi\rho} \quad . \] (1.90)

The solution for \( \psi(k_o | r) \) can now be given as a sum of the particular integral generated by \( G \) and a solution of the homogeneous equation,

\[ \psi(k_o | r) = e^{ik_o \cdot \vec{r}} - \frac{1}{4\pi} \int |r - r'|^{-1} e^{ik_o \cdot |r - r'|} U(r') \psi(k_o | r') dr' \quad . \] (1.91)

By looking at the asymptotic form of this expression, it will be possible to verify Eq. (1.27) and at the same time obtain a definition of \( f_o \).

To this end, the following approximation is needed:

\[ |r - r'| = (r^2 - 2r \cdot r' + r')^\frac{1}{2} \sim r - r' + \cdots, \quad r \gg r' \quad . \] (1.92)

Using this in Eq. (1.91) gives

\[ \psi(k_o | r) \sim e^{ik_o \cdot \vec{r}} + e^{ikr} \left( -\frac{1}{4\pi} \int e^{-ik_o \cdot \vec{r}'} U(r') \psi(k_o | r') dr' \right) \] (1.93)

Note that the quantity \( k_o \cdot \vec{r} \) appearing in the exponential is just the scattered wave vector \( k_o \) (magnitude \( k_o \), direction \( \hat{r} \)). Thus, the scattering amplitude is given by

\[ f_o (\hat{r}) \equiv f_o (k_o) = -\frac{1}{4\pi} \int e^{-ik_o \cdot \vec{r}} U(r) \psi(k_o | r') dr' \quad . \] (1.94)

If one attempts the solution of Eq. (1.91) by iteration, the first approximation is

\[ \psi(k_o | r) \approx e^{ik_o \cdot \vec{r}} \quad , \] (1.95)

which leads to the Born approximation for the scattering amplitude,

\[ f_o (\hat{k}) = -\frac{1}{4\pi} \int e^{i(k_o - k) \cdot \vec{r}'} U(r') dr' \quad . \] (1.96)
This expression finds such wide use that a few additional comments should be made. The vector

$$\tilde{\mathbf{h}} K \equiv \tilde{\mathbf{h}}(k - k_o)$$

(1.97)
gives the momentum transferred by the collision, and it is evident that this completely determines $f_o$ in this approximation. Carrying out the angular integral as before, one obtains

$$f_o(K) = -\frac{1}{K} \int_0^{\infty} r' \sin Kr' U(r')dr'$$

(1.98)

for spherical potentials. From Eq. (1.97), the magnitude $K$ can be related directly to the scattering angle $\theta$ by

$$K = 2k_o \sin (\frac{\theta}{2}).$$

(1.99)

This concludes the discussion of elastic scattering.
2. MULTICHANNEL SCATTERING

Scattering Process, Cross Sections, and Coupled Equations

The prototype scattering system examined in this section consists of a simple projectile and a structured target. Obviously the considerations here deal directly with the theory of electron-hydrogen atom scattering. By a "structured target" is meant a subsystem \( A \) in the problem, with a set of coordinates \( \{ \rho \} \) relative to the center of mass of \( A \), which satisfies an internal Schrödinger equation

\[
H_{a}(\rho) \hat{\phi}_{a}(\rho) = E_{a} \hat{\phi}_{a}(\rho).
\]  

(2.1)

This equation determines the discrete and continuous energies \( E_{a} \) and orthonormal eigenstates \( \hat{\phi}_{a} \) of the target. The energy scale will be assumed to be shifted so that for the ground state \( \phi_{0} \) we have \( E_{0} = 0 \).

For simplicity assume that the target is massive enough, relative to the projectile, that the center of mass of the target and the center of mass of the entire system coincide. The reduced mass of the system with respect to relative motion will then be just the mass of the projectile. Thus, the Schrödinger equation for the system with the center of mass motion omitted is

\[
[(-\hbar^{2}/2m)\nabla_{r}^{2} + H_{a}(\rho) - E] \psi_{\rho}(r,\rho) = -V(r,\rho) \psi_{\rho}(r,\rho),
\]

(2.2)

where \( r \) is the relative coordinate between the projectile and \( A \), and \( V(r,\rho) \) is the interaction between projectile and target. As before, it will be assumed that
\[ V(r,\rho) \approx 0, \quad r > \bar{R}, \] (2.3)

which statement does not depend on the target configuration \( \rho \).

If \( V \) were identically zero, then the Hamiltonians of the projectile and target would be strictly additive. Eigenstates of the system would then be represented by simple product functions of the form

\[
\begin{align*}
&\frac{ik \cdot r}{e^{-\alpha}} \phi_\alpha(\rho), \quad (2.4a) \\
&\frac{r^{-1}}{H_{2}^{(+)}(k \cdot r)} Y_{\rho m}(\hat{r}) \phi_\alpha(\rho), \quad (2.4b)
\end{align*}
\]

where energy conservation requires that the wave vectors \( k_\alpha \) satisfy

\[ E_\alpha + \frac{\hbar^2}{2m} k_\alpha^2 = E \]
(2.5)

for all \( \alpha \). In actual fact, such states are what are really observed, since any observation in the scattering problem is always made at \( r \gg \bar{R} \), and the true wavefunction there must be expressible as a linear combination of states such as those in Eq. (2.4). The technical jargon for any of the product states is "channel". States for which \( E - E_\alpha \) is negative are called "closed channels", since a particle with an imaginary wave vector cannot propagate and must decay exponentially. Thus, there will be no flux at infinity for such a channel. Channels for which \( E - E_\alpha > 0 \) are "open channels". For a fixed energy \( E \) below the continuum of \( A \), there are only particular values that the open channel \( k_\alpha \) can have, since the \( E_\alpha \) in Eq. (2.5) will be discrete. Scattering processes for which \( E \) lies in the continuum of \( A \) will not be considered.
Our intuitive description of the collision process is as follows.

1) For A in a particular state $E_{\alpha}$, the projectile is shot at it with wavenumber $k_{\alpha}$. This determines the total energy $E = E_{\alpha} + \frac{\hbar^2 k_{\alpha}^2}{2m}$.

2) When the projectile gets to the target vicinity, the interaction $V$ couples the two subsystems. During this time, the direction of $k_{\alpha}$ may be changed, and more importantly, energy may be transferred to A, exciting it to a higher state $E_{\alpha'}$. This leaves the projectile with energy $\frac{\hbar^2 k_{\alpha}'^2}{2m} = (E_{\alpha} - E_{\alpha'}) + \frac{\hbar^2 k_{\alpha}^2}{2m} = E - E_{\alpha'}$. It is evident that $E_{\alpha'}$ must be less than $E$ if the projectile is to leave the target region. Note that this does not preclude, however, the possibility of "virtual excitations", that is, temporary excitations of states with $E_{\alpha'} > E$. All that is required is that when the projectile leaves, A must be in a state $\alpha'$ with $E_{\alpha'}, < E$.

3) Finally, the projectile is detected with some propagation vector $k_{\alpha'}$.

A concise description of the development of the system is to say that it starts in some incident channel $\alpha$, then due to $V$ shuffles around among all possible channels $\{\alpha\}$, and finally ends in one of the allowed (open) channels $\alpha'$. The asymptotic wavefunction embodying this description, in analogy with Eq. (1.27), is

$$\psi_{\alpha}(r, \rho) \sim e^{-ik_{\alpha} \cdot r} \phi_{\alpha}(\rho) + \sum_{\alpha'} f_{\alpha \alpha'}(k_{\alpha}, \hat{k}_{\alpha}) \frac{e^{ik_{\alpha'} \cdot r}}{r} \phi_{\alpha'}(\rho).$$

Note that $\psi$ is subscripted by $\alpha$ to denote the incident channel, both the state $\phi_{\alpha}$ and wave vector $k_{\alpha}$. In addition, $f_{\alpha \alpha'}$ is explicitly indicated.
to depend on the directions of both \( k_\alpha \) and \( k_\alpha' \). Of course, \( \psi \) and \( f_{\alpha\alpha'} \) both depend on \( E \), which is a constant for the problem.

The definition of cross sections is only slightly more complex than before. One now considers the flux scattered into the element of solid angle \( d\Omega \) along the channel wave vector \( k_\alpha' \), with the target in state \( \phi_\alpha' \), compared to the flux incident on the target in channel \( \alpha \). In analogy with Eq. (1.31), the differential cross section for this process is

\[
\frac{d\sigma_{\alpha\alpha',(k_\alpha',k_\alpha')}}{d\Omega} = \frac{k_\alpha'}{k_\alpha} |f_{\alpha\alpha',(k_\alpha',k_\alpha')}|^2 .
\]  

(2.7)

Again, \( f_{\alpha\alpha'} \) is called the scattering amplitude for the process just described, and it is found by comparing the actual solutions of Eq. (2.2) with the asymptotic form in Eq. (2.6).

The Schrödinger equation can be reduced to an equation just involving the scattering coordinate \( \rho \). This is done by recognizing that the \( \phi_\alpha \) provide a basis for expanding any function of \( \rho \) (in the same function space). Thus, the full wavefunction can be expanded as

\[
\psi_\alpha(\rho,\rho') = \sum_{\alpha'} \phi_{\alpha'}(\rho') \psi_{\alpha'}(\rho) .
\]  

(2.8)

where \( \alpha' \) runs over all states of \( A \), including the continuum. Comparison of this expression with Eq. (2.6) shows that the scattering functions \( \psi_{\alpha'\alpha} \) must have the asymptotic form

\[
\psi_{\alpha'\alpha}(\rho) \sim e^{\pm i k_\alpha' \cdot \rho} + f_{\alpha\alpha',(k_\alpha',k_\alpha')} \frac{e^{i k_\alpha \cdot \rho}}{\rho} .
\]  

(2.9a)
if $\alpha'$ is an open channel, and

$$\psi_{\alpha',\alpha}(r) \sim g_{\alpha',\alpha}(k_{\alpha'}, k_{\alpha}) \frac{\mathrm{e}^{-\mathbf{k}_{\alpha'} \cdot r}}{r}$$

(2.9b)

if $\alpha'$ is a closed channel, where the replacement $k_{\alpha} \rightarrow iK_{\alpha'}$ has been made for the imaginary wave number. This form can be justified from the integral equation developed later for $\psi_{\alpha}$.

The equations which the scattering functions must satisfy are found the following way. Write the Schrödinger equation for the full wavefunction with a particular incident channel $\alpha^0$,

$$\sum_{\alpha'} \left[ (-\hbar^2/2m) V_x^2 + H_a(\rho) - E \right] \phi_{\alpha',\alpha}(\rho) \psi_{\alpha',\alpha^0}(r)$$

$$= -\sum_{\alpha'} V(r,\rho) \phi_{\alpha',\alpha}(\rho) \psi_{\alpha',\alpha^0}(r)$$

(2.10)

If this equation is multiplied on the left by $\phi_{\alpha^0}(\rho)$ and integrated over $\rho$, the result is

$$(V_x^2 + k_{\alpha}^2) \psi_{\alpha\alpha^0}(r) = \sum_{\alpha'} U_{\alpha\alpha'}(r) \psi_{\alpha',\alpha^0}(r)$$

(2.11)

where the orthonormality of the $\phi_{\alpha}$ has been used on the left, and the matrix elements of the potential are

$$U_{\alpha\alpha'}(r) = \frac{2m}{\hbar^2} \int \phi_{\alpha^0}^*(\rho) V(r,\rho) \phi_{\alpha'}(\rho) \, d\rho.$$  

(2.12)

It is seen that each scattering function depends on all the others, and in very complicated ways. In certain cases, the potential matrix may take on a block diagonal form, which helps considerably, but in general, Eq. (2.11) represents an infinite set of coupled channels.
Another important observation is that from the standpoint of the differential equations, the index $\alpha^0$ is superfluous, that is, there is nothing in the equations themselves which will introduce $\alpha^0$ as the incident channel. Both of the points just noted will be discussed in detail later.

Extended Partial Wave Analysis

It is useful now to extend the partial wave treatment of the last section to the more complicated problem at hand. One change is that the incident direction may not have much significance for the subsystem A, so formulae will be written with all directions implicit in them. For example, $f_{\alpha\alpha', (\hat{k}_\alpha, \hat{k}_{\alpha'})}$ may depend explicitly on both the directions $\hat{k}_\alpha$ and $\hat{k}_{\alpha'}$, and not just on their relative directions. It will therefore be expanded in terms of a complete set of spherical harmonics for each direction,

$$f_{\alpha\alpha', (\hat{k}_\alpha, \hat{k}_{\alpha'})} = \sum_{\ell m} \sum_{\ell' m'} 2\pi (k_\alpha k_{\alpha'})^{-\ell} i^{\ell - \ell' + 1}$$

$$\times T(\alpha \ell m | \alpha' \ell' m') Y_{\ell m}^*(\hat{k}_\alpha) Y_{\ell' m'}^*(\hat{k}_{\alpha'})$$

(2.13)

where the expansion factors have been denoted by $T$, and the numerical factors have been included for convenience later. As in Section 1, this formula will be used in an expansion of the asymptotic form of $r \psi_{\alpha, a}(r)$. To make the later algebra easier, it is useful to employ a modified form of the plane wave expansion, with a dummy summation constructed so as to resemble Eq. (2.13),
\[ \frac{\mathbf{ik} \cdot \mathbf{r}}{r e^{-\alpha \delta_{\alpha,\alpha'}}} = \sum_{\ell m} \sum_{\ell' m'} \delta(\alpha \ell m | \alpha' \ell' m') 4\pi(k \mathbf{k} \cdot \mathbf{r})^{-\frac{\ell}{2}} i^\ell F_\ell(k \mathbf{r}) Y_{\ell m}^*(\mathbf{k'} \mathbf{r}) Y_{\ell' m'}(\mathbf{r}). \] (2.14)

The abbreviation \( \delta(\alpha \ell m | \alpha' \ell' m') = \delta_{\alpha,\alpha'} \delta_{\ell,\ell'} \delta_{m,m'} \), has been used. The asymptotic form of the Ricatti-Bessel function which will be used is

\[ F_\ell(k \mathbf{r}) \sim \frac{1}{2i} \left[ \exp i(k \mathbf{r} - \ell \pi/2) - \exp -i(k \mathbf{r} - \ell \pi/2) \right]. \] (2.15)

The next step is to substitute Eqs. (2.13) - (2.15) into Eq. (2.9). Again, recognize that the asymptotic form is being examined at the detector where \( \mathbf{r} = \mathbf{k'}. \) The final form is

\[
\psi_{\alpha\alpha'}(r) \sim \sum_{\ell m} \sum_{\ell' m'} 2\pi(k \mathbf{k} \cdot \mathbf{r})^{-\frac{\ell}{2}} i^{\ell+1} Y_{\ell m}^*(\mathbf{k'}) Y_{\ell' m'}(\mathbf{k'})
\]

\[
\times \left[ \delta(\alpha \ell m | \alpha' \ell' m') \exp -i(k \mathbf{r} - \ell' \pi/2) 
- S(\alpha \ell m | \alpha' \ell' m') \exp -i(k \mathbf{r} - \ell' \pi/2) \right], \] (2.16)

where the "S-matrix", defined by

\[ S(\alpha \ell m | \alpha' \ell' m') = \delta(\alpha \ell m | \alpha' \ell' m') - T(\alpha \ell m | \alpha' \ell' m'), \] (2.17)

has been introduced. A word about Eq. (2.17) is in order. Several relationships between S and T may be seen in books and the literature, differing from this one usually by factors of \( i \) and \( 2\pi \). None of these is more correct than the others. The differences arise solely as a result of the factors introduced in Eq. (2.13), and this is purely
arbitrary. All that is required is that any particular development of these equations be self-consistent.

It is now possible to state explicitly the partial wave expansion of the total wavefunction, based on Eqs. (2.8) and (2.16). The expansion is in two parts: first,

\[ \psi_{\alpha}(r, \rho) = \sum_{\ell m} \frac{1}{\ell + 1} \psi_{\ell m}(r, \rho) Y_{\ell m}^* \hat{k}_{\alpha} \]  

(2.18)

which takes care of the direction of the incident wave; and second,

\[ \psi_{\alpha\ell m}(r, \rho) = \sum_{\ell', m'} \left( \sum_{\alpha', \ell', m'} r^{-1} U_{\alpha\ell m, \alpha' \ell' m'}(r) Y_{\ell', m'}(r) \hat{\phi}_{\alpha'}(\rho) \right) \]  

(2.19)

The radial functions \( U_{\alpha\ell m, \alpha' \ell' m'}(r) \) describe the scattering from channel \( \alpha \ell m \) to \( \alpha' \ell' m' \), and for open channels are required to have the asymptotic form

\[ U_{\alpha \ell m, \alpha' \ell' m'}(r) \sim k_{\alpha}^{-\frac{1}{2}} \left[ \delta(\alpha \ell m | \alpha' \ell' m') \exp -i(k_{\alpha} r - \ell \pi / 2) \right. \]

\[ \left. - S(\alpha \ell m | \alpha' \ell' m') \exp i(k_{\alpha} r - \ell' \pi / 2) \right] . \]  

(2.20)

A useful convention is to introduce the collective label \( \Gamma \equiv (\alpha, \ell, m) \), which is called a channel index. Equation (2.20) may then be expressed compactly as

\[ U_{\Gamma, \Gamma'}(r) \sim k_{\Gamma}^{-\frac{1}{2}} \left[ \delta_{\Gamma, \Gamma'} \exp -i(k_{\alpha} r - \ell \pi / 2) \right. \]

\[ \left. - S_{\Gamma, \Gamma'} \exp i(k_{\alpha} r - \ell' \pi / 2) \right] . \]  

(2.21)

One sees that in the partial wave framework the ordinary channel label \( \alpha \) is supplemented by the \( \ell, m \) expansion indices to form the partial wave channel label \( \Gamma \). Coupled equations similar to those in Eq. (2.11) will be derived later for the radial functions \( U_{\Gamma, \Gamma'} \).
For a given incident wave vector, \( k_\alpha \), the total cross section for the target excitation \( \alpha \rightarrow \alpha' \) is found from the partial wave analysis by substituting Eq. (2.13) into Eq. (2.7) and integrating over all scattering angles. Thus,

\[
\sigma_{\alpha \alpha'}(\hat{k}_\alpha) = \left( \frac{k_{\alpha}'}{k_\alpha} \right) \int f_{\alpha \alpha'}(\hat{k}_\alpha \hat{k}_{\alpha'}) d\hat{k}_{\alpha'} \nonumber \]

\[
= \left( \frac{4\pi^2}{k_\alpha^2} \right) \sum_{\ell_o, m_o, \ell, m} \ell \ell' m m' T(\alpha \ell_o m_o | \alpha' \ell' m') T^*(\alpha \ell m | \alpha' \ell' m'). \nonumber \]

(2.22)

This expression may be further averaged over all directions of incidence to give the total cross section at this energy

\[
\sigma(\alpha \rightarrow \alpha') = \frac{1}{4\pi} \int \sigma_{\alpha \alpha'}(\hat{k}_\alpha) d\hat{k}_\alpha \nonumber \]

\[
= \left( \frac{\pi}{k_\alpha^2} \right) \sum_{\ell, m} \sum_{\ell', m'} |T(\alpha \ell m | \alpha' \ell' m')|^2. \nonumber \]

(2.23)

This last expression describes the cases:

1) fixed target, random \( \hat{k}_\alpha \) (the target is surrounded by a swarm of projectiles);

2) fixed \( \hat{k}_\alpha \), random orientations of the target.

It should be noted that the S-matrix can be proved to be symmetric. Thus, the T-matrix is symmetric also, and one has the micro-reversibility condition that

\[
k_\alpha^2 \sigma(\alpha \rightarrow \alpha') = k_{\alpha'}^2 \sigma(\alpha' \rightarrow \alpha).
\]

Green Function for the Multichannel Case

The Green function which will be used to cast Eq. (2.2) into integral equation form can be defined by

\[
[v^2 + (2\mu/h^2)(H_a - E)] G(\bar{r}, \bar{r}' | \bar{\rho}, \bar{\rho}') = \delta(\bar{r} - \bar{r}') \delta(\bar{\rho} - \bar{\rho}'). \nonumber \]

(2.24)
Proceeding as before, the delta function in \( r \) and \( r' \) may be written as a Fourier integral. The delta function in target coordinates is given by the completeness relation

\[
\delta(\rho - \rho') = \sum_{\alpha} \phi_{\alpha}^{*}(\rho) \phi_{\alpha}(\rho') ,
\]

where the sum over all \( \alpha \) is meant to include integration over any continuum. The Green function will be constructed from the expansion

\[
G(r - r'|\rho,\rho'|) = \sum_{\alpha} \int_{\sim} dk g_{\alpha}(k) e^{\frac{ik\cdot(r-r')}}{\sim} \phi_{\alpha}(\rho) \phi_{\alpha}^{*}(\rho') .
\]

Equation (2.24) serves to define the kernels \( g_{\alpha}(k) \) by

\[
g_{\alpha}(k) = \left(\frac{1}{2\pi}\right)^{3} (k_{\alpha}^{2} - k^{2})^{-1} .
\]

The \( \sim \)-integration in Eq. (2.26) may be carried out by treating each pair of poles, \( k = \pm k_{\alpha} \), as before. Using the resulting Green function to include the inhomogeneity on the right hand side of Eq. (2.2) gives the following integral equation for the full wavefunction,

\[
\psi_{\alpha}^{(\gamma,\rho)} = e^{\frac{ik_{\alpha}\cdot r}{\sim}} \phi_{\alpha}(\rho) - \frac{1}{4\pi} \sum_{\alpha} \phi_{\alpha}(\rho)
\]

\[
\times \int \frac{dr'd\rho'}{|r-r'|^{-1}} e^{\frac{ik_{\alpha}\cdot |r-r'|}{\sim}} \phi_{\alpha}^{*}(\rho') U(\rho',\rho) \psi_{\alpha}(\rho,\rho') dr'd\rho' .
\]

As long as \( E \) has been restricted to lie below threshold (continuum of \( A \)), it is seen that the asymptotic form of this equation as \( r \to \infty \) is just Eq. (2.6), with the scattering amplitudes identified as

\[
f_{\alpha\alpha}^{\hat{k}_{\alpha},\hat{k}_{\alpha}}(\rho,\rho') = -\frac{1}{4\pi} \int_{\sim} e^{-\frac{i k_{\alpha}\cdot |r-r'|}{\sim}} \phi_{\alpha}(\rho') U(\rho,\rho') \psi_{\alpha}(\rho,\rho') dr'd\rho' .
\]
Of course, this is only an implicit definition of $f_{\alpha \ell}$, since $\psi_{\alpha}$ appears under the integral. It may still be of use, however, if the conditions of the problem suggest that a Born approximation may be used. From Eq. (2.28), the wavefunction is approximated by

$$\psi_{\alpha}(r, \rho) \approx e^{\frac{i k_{\alpha}}{r} \cdot \hat{r}} \phi_{\alpha}(\rho),$$  \hspace{1cm} (2.30)

and using this in Eq. (2.29),

$$f_{\alpha \ell} \approx \left( \frac{k_{\alpha}}{\rho} \right) \frac{1}{4\pi} \int e^{i \frac{(k_{\alpha} - k_{\alpha}^{'}) \cdot \hat{r}'}} U_{\alpha \ell} \phi_{\alpha}(r', \rho) \, dr',$$  \hspace{1cm} (2.31)

where $U_{\alpha \ell}$ is defined in Eq. (2.12).

Close Coupled Approximation

From Eq. (2.18), it can be seen that for any $\alpha, \ell, m$, the function $\psi_{\alpha \ell m}(r, \rho)$ satisfies Eq. (2.2). A procedure similar to the one leading to Eqs. (2.10) and (2.11) may be used to find the equations satisfied by the radial functions $U_{\Gamma r}$. One starts with the equation

$$\int Y_{\ell m}^* \Phi_{\alpha}^* \rho \left( \frac{-h^2}{2m} \nabla_r^2 + H_{\alpha}(\rho) - E + V(r, \rho) \right) \psi_{\alpha \ell m}(r, \rho) \, dr \, d\rho = 0$$  \hspace{1cm} (2.32)

where a particular incident channel $\Gamma^0 = (\alpha^0, \ell^0, m^0)$ has been selected.

Introducing the expansion from Eq. (2.19) into this integral and performing the integrations leads to the set of coupled equations,

$$\left[ \frac{d^2}{dr^2} + k_{\alpha}^2 - \frac{\ell (\ell + 1)}{r^2} \right] U_{\Gamma r} (r) = \sum_{\Gamma'} U_{\Gamma \Gamma'} (r) U_{\Gamma r}^{\Gamma^0} (r),$$  \hspace{1cm} (2.33)

where $\Gamma'$ runs over all possible channels.
The potential functions are given by
\[
U_{\Gamma \Gamma'}(r) \equiv \int \hat{Y}_{\ell m}^*(\hat{r}) \ U_{\alpha \alpha'}(r) \ \hat{Y}_{\ell' m'}(\hat{r}) \ d\hat{r}.
\]  
(2.34)

In terms of obtaining an exact numerical solution of the scattering problem, there are several grim alternatives:

1) a six-dimensional integration of Eq. (2.2);

2) a three-dimensional integration of the infinite set of equations in Eq. (2.11);

3) a one-dimensional integration of the even larger set of equations in Eq. (2.33).

Obviously, approximations must be made if any results at all (even bad ones) are to be obtained. The method to be discussed here is the close coupled approximation applied to alternative 3). This approximation consists of including only a finite (and usually small) number of terms in Eq. (2.19). The possibility of neglecting the higher \( \ell \) values was discussed in Section 1, but the close coupled approximation contends further that only nearby target states \( \alpha' \) are important in describing transitions to state \( \alpha \). For instance, if one wishes to study the 1s - 2s transition induced in atomic hydrogen by electron bombardment, the argument is that in addition to the 1s and 2s basis states, perhaps only the 2p state needs to be included in the sum over \( \alpha' \) in order to describe the atomic state during this process. The assumption is that the coupling matrix elements \( U_{\alpha \alpha'} \) will be very small between these states and any higher atomic states.
With any truncation of Eq. (2.19), the resulting series cannot reproduce the exact wave function \( \psi \), but it gives a function \( \psi^t \) whose deviation \( \delta \psi = \psi - \psi^t \) may be small. Variational methods in scattering theory have been used to investigate the error that \( \delta \psi \) introduces into the calculated scattering amplitudes. It is found that the amplitudes \( f^t_{\alpha \alpha} \) calculated from \( \psi^t \) will differ from the exact ones \( f_{\alpha \alpha} \), by

\[
f^t_{\alpha \alpha} - f_{\alpha \alpha} = O((\delta \psi)^2),
\]

(2.35)

that is, by terms which are quadratic in the variation \( \delta \psi \). This result requires that \( \psi^t \) satisfy the Hartree-Fock equation, Eq. (2.32). Thus, if terms are chosen in Eq. (2.19) which result in a reasonably accurate description of \( \psi \), then scattering amplitudes calculated from the truncated (finite) set of coupled equations, Eq. (2.33), may be fairly accurate. Relations similar to Eq. (2.35) can also be found for the T-matrix elements.

We turn now to the consideration of how the approximate T-matrix can be constructed from the solutions of the coupled radial equations. It will be assumed that the only channels included in the sum over \( \Gamma' \) are open channels. Equations (2.33) are seen to have the properties noted for Eq. (2.11); in particular, the incident channel specification \( \Gamma^o \) is superfluous. That is, there is no "built in" incident channel. The \( \Gamma^o \) specification is one which is to be forced onto the radial functions. This is done the following way.

Suppose there are \( n \) functions being included in the close coupled approximation. Then the \( n \) equations

\[
\left[ \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2_{\Gamma} \right] f_{\Gamma}(r) = \sum_{\Gamma'} U_{\Gamma \Gamma'}(r)f_{\Gamma'}(r)
\]

(2.36)
are solved for some arbitrary set of initial conditions on the n first
derivatives of the radial functions \( f_\Gamma \). The initial conditions on the
functions themselves are

\[
f_\Gamma(0) = 0, \text{ all } \Gamma. \tag{2.37}
\]

The set of solutions so obtained are called the set \( f^{(1)} \). The equations
are then solved again with a set of initial conditions which generates a
second set of solutions \( f^{(2)} \), linearly independent of \( f^{(1)} \). It is
obvious that there are n such sets, \( f^{(i)} \), \( i = 1, n \). None of these will
have the asymptotic form required in Eq. (2.21), but it will be possible
to take n linear combinations of the sets \( f^{(i)} \) which will have the re-
quired form.

For example, it will be seen in Chapters Two and Three that sets of
solutions can be generated by the noniterative integral equation technique
of Sams and Kouri which have the asymptotic form

\[
f_\Gamma^{(\Gamma')} (r) \sim k_\Gamma^{-1} \left[ \delta^{\Gamma}_{\Gamma'} \sin(k_\Gamma r - \ell \pi / 2) + R^{\Gamma}_{\Gamma'} \cos(k_\Gamma r - \ell \pi / 2) \right]. \tag{2.38}
\]

It can be seen from Eq. (2.21) that the desired functions can be written

\[
U^{\Gamma_o}_{\Gamma} (r) \sim k_\Gamma^{-1} \\
\times \left[ -i(\delta^{\Gamma_o}_{\Gamma} + S^{\Gamma_o}_{\Gamma}) \sin(k_\Gamma r - \ell \pi / 2) + (\delta^{\Gamma_o}_{\Gamma} - S^{\Gamma_o}_{\Gamma}) \cos(k_\Gamma r - \ell \pi / 2) \right]. \tag{2.39}
\]

Thus, the linear transformation between the two sets of solutions is

\[
U^{\Gamma_o}_{\Gamma} = -i \sum_{\Gamma'} \left( \delta^{\Gamma_o}_{\Gamma'} + S^{\Gamma_o}_{\Gamma'} \right) f^{(\Gamma')}_{\Gamma} \\
= -i(\delta^{\Gamma_o}_{\Gamma} + S^{\Gamma_o}_{\Gamma}) \sin(k_\Gamma r - \ell \pi / 2) \\
+ \left[ \sum_{\Gamma'} (-1)(\delta^{\Gamma_o}_{\Gamma'} + S^{\Gamma_o}_{\Gamma'}) R^{\Gamma}_{\Gamma'} \right] \cos(k_\Gamma r - \ell \pi / 2). \tag{2.40}
\]
Comparing this with Eq. (2.39) shows that the S coefficients must satisfy

\[ \sum_{\Gamma'} (\delta_{\Gamma'\Gamma}^0, + S_{\Gamma'\Gamma}^0, \Gamma_{\Gamma'}^0, \Gamma_{\Gamma'}^0) \Gamma_{\Gamma'}^0, \Gamma_{\Gamma'}^0 = i(\delta_{\Gamma'\Gamma}^0 - S_{\Gamma'\Gamma}^0, \Gamma_{\Gamma'}^0, \Gamma_{\Gamma'}^0, \Gamma_{\Gamma'}^0), \]  

(2.41)

which can be written in matrix form

\[ (1 + S) \cdot \Gamma_{\Gamma'} = i(1 - S). \]  

(2.42)

This may be solved for S to give

\[ S = (1 + i\Gamma) \cdot (1 - i\Gamma)^{-1}. \]  

(2.43)

In summary, an actual calculation proceeds in the following manner. Equations (2.36) are solved n times to generate the linearly independent sets \( f^{(1)} \), \( i = 1, n \), with conditions fixed so that the asymptotic forms in Eq. (2.38) are obtained. If the \( f^{(1)} \) do not give this form, linear combinations of them will. (Note throughout this discussion the use of real functions in the actual numerical calculations.) The "reactance matrix" elements \( R_{\Gamma'\Gamma} \) which are derived from these functions are used to calculate the "transition matrix" \( T \) from

\[ T = 1 - S = 2i\Gamma \cdot (1 - i\Gamma)^{-1}. \]  

(2.44)

Finally, the T-matrix elements are used in Eq. (2.13) to get the actual scattering amplitudes, or Eq. (2.23) to get the total cross sections.

The work discussed in Chapter Two has for its goal the construction of the \( f^{(1)} \) sets for the problem of electron impact on atomic hydrogen with electron exchange terms included. The explicit background for the calculation is the subject of the next section. Notable in Chapter Two is the use of an integral equation technique which gives precisely the asymptotic form in Eq. (2.38).
3. ELECTRON-HYDROGEN ATOM SCATTERING

The major purpose of this section is to derive explicit formulae (which usually appear in the literature in very schematic form) for the application of the results of the last section to the special case where the projectile is an electron and the target is a hydrogen atom. Several interesting further concepts also come into play, particularly the use of a coupled basis set and an antisymmetrized scattering function to allow for exchange of the two electrons.

For this system, the center of mass is taken to be at the proton. The coordinate \( \mathbf{r}_v \) is then just the position vector of the atomic electron, and \( \mathbf{r}_\lambda \) the position vector of the scattered electron, both relative to the proton. The eigenfunctions of the target Hamiltonian, \( H_a \), are the normalized hydrogen wavefunctions

\[
\phi_{\alpha \lambda} (\mathbf{r}, \mathbf{p}) = R_{\nu \lambda} (\mathbf{r}) Y_{\lambda \mu} (\mathbf{p}).
\]  

(3.1)

In order to keep the notation straight, the \( \alpha \) quantum numbers will be written explicitly as \( \nu, \lambda, \mu \). Also, the channel wave number will be denoted by \( k_{\nu} \), since the atomic energy is just a function of \( \nu \). Using a very detailed notation, Eqs. (2.18) and (2.19) are written

\[
\psi_{\nu \mu \lambda \lambda'} (\mathbf{r}, \mathbf{p}) = \sum_{\lambda m} 2\pi k_{\nu}^{-L} L^{L+1} \psi_{\nu \mu \lambda \lambda'} (\mathbf{r}, \mathbf{p}) Y_{Lm} (k_{\nu}),
\]  

(3.2)

\[
\psi_{\nu \mu \lambda \lambda'} (\mathbf{r}, \mathbf{p}) = \sum_{\lambda ' \lambda '', \lambda ' ' \mu ' \mu ' ' m ' m } \psi_{\nu \lambda ' \mu ' \lambda ' ' \mu ' ' m ' m ' ' (r)Y_{Lm ' m ' ' (r)} Y_{\lambda ' \mu ' ' (r)} R_{\nu \lambda} (\mathbf{p}).
\]  

(3.3)
Coupled Basis

At this point it is very useful to note a particular symmetry property of the full Hamiltonian

\[ H(r, \rho) = (-\hbar^2/2m) \left[ \nabla_r^2 + \nabla_\rho^2 \right] - e^2 |r^{-1} + \rho^{-1}| + e^2 |r - \rho|^{-1}, \tag{3.4} \]

namely, it is invariant to rotations of the system as a whole. Thus, the total angular momentum \( L = (L_r + L_\rho) \) commutes with \( H \), and \( L^2 \) and the z-component \( L_z \) (quantum numbers \( L \) and \( M \)) provide good quantum numbers. It is therefore possible to do the scattering calculations in a basis which is diagonal in \( L \) and \( M \). The motivation for this is that the infinite set of coupled equations for the \( U_{\Gamma}^{\pi,i} \) functions will break up into sets associated with each given \( L \) (the magnetic quantum number will be found not to matter). This is an example of the blocking of the potential matrix which was mentioned after Eq. (2.12).

Following the usual scheme of coupling two angular momenta, a new set of angular basis functions are defined as follows:

\[ Y_{\ell \lambda,LM}^{\hat{r},\hat{\rho}} = \sum_{\mu \nu} C(\ell \lambda L | m \mu M) Y_{\lambda m}^{\hat{r}} (r) Y_{\lambda \mu}^{\hat{\rho}} (\rho), \tag{3.5} \]

where the \( C \)'s are Clebsch-Gordan coefficients. It will be useful to have a statement of the orthogonality relations

\[ \sum_{LM} C(\ell \lambda L | m \mu M) C(\ell \lambda L' | m' \mu' M') = \delta_{m, m'} \delta_{\mu, \mu'}, \tag{3.6a} \]

\[ \sum_{m \mu} C(\ell \lambda L | m \mu M) C(\ell \lambda L' | m' \mu M') = \delta_{M, M'} \delta_{L, L'}, \tag{3.6b} \]

where the second of these is subject to the requirement that \((\ell, \lambda, L)\) obey a triangle inequality.
A new set of scattering functions may be defined in this basis by

\[ \psi_{\nu \lambda \ell LM}(r, \rho) = \sum_{\nu' \lambda' \ell'} r^{-1} U_{\nu' \lambda' \ell'}^{\nu \lambda \ell LM}(r) \psi_{\lambda' \ell' LM}(r, \rho) R_{\nu', \lambda', \ell'}(\rho). \]  

(3.7)

Notice that one need not write a summation over \( L' \) and \( M' \) here, with summand subscripts \( L' \) and \( M' \), to take the place of the \( m', \mu' \) sums in Eq. (3.3). This is because the equations for the expansion function \( U \) will be diagonal in \( L \) and \( M \), as already pointed out.

The asymptotic form of these new radial functions will be assumed to be

\[ U_{\nu' \lambda' \ell'}^{\nu \lambda \ell LM}(r) \sim k_{\nu'}^{-\ell'} \]

\[ \times \left[ \delta(\nu' \lambda' | \nu \lambda \ell \ell') \exp -i(k_{\nu'} r - \ell' \pi/2) - S_{LM}^{LM}(\nu \lambda \ell | \nu' \lambda' \ell') \right. \]

\[ \times \left. \exp i \left( k_{\nu'} r - \ell' \pi/2 \right) \right], \]  

(3.8)

which defines the S-matrix in this representation. In order to make use of these functions, it is necessary to see

1) how they are related to the old ones, and

2) what equations they satisfy.

These two questions will be answered in order in the rest of this section.

Relation Between Coupled and Uncoupled Representations

and the Radial Equations

We can see that the functions we want, \( \psi_{\nu \lambda \mu m} \), depend on \( \mu \) and \( m \). These were the quantum numbers summed over to generate the \( L, M \) representation. Thus, we expect that in order to get back to the \( \mu, m \) representation,
a sum over \( L \) and \( M \) will be required; thus,

\[
\psi_{\nu\lambda\mu\ell m} = \sum_{LM} B(\lambda\mu\ell mLM) \psi_{\nu\lambda\ell LM} . \tag{3.9}
\]

The \( B \) coefficients can be determined by requiring that the asymptotic form of Eq. (3.9) be identical with that of Eq. (3.3). Using Eq. (20) in Eq. (3.3) gives

\[
x_{\nu\lambda\mu \ell m}(r, \rho) \sim \sum_{\nu', \lambda', \ell', \mu'} Y_{\nu'}(r, \rho) Y_{\lambda'}(r, \rho) R_{\nu', \lambda', \ell', \mu'}(\rho) k_{\nu'}^{-\ell'} - \frac{1}{S(\nu\lambda\mu \ell m|\nu'\lambda'\ell'\mu')} \exp \left[ i\left( k_{\nu'} r - \ell' \pi/2 \right) \right]. \tag{3.10}
\]

Equation (3.7) may be substituted into Eq. (3.9), and when Eqs. (3.5) and (3.8) are employed, one finds

\[
x_{\nu\lambda\mu \ell m} \sim \sum_{\nu', \lambda', \ell', \mu'} Y_{\nu'}(r, \rho) Y_{\lambda'}(r, \rho) R_{\nu', \lambda', \ell', \mu'}(\rho) k_{\nu'}^{-\ell'}
\]

\[
\times \left[ \frac{1}{B(\lambda\mu\ell mLM) C(\lambda\ell' L|\mu' m'M)} \delta(\nu\lambda\ell m|\nu'\lambda' \ell' \mu') \exp \left[ i\left( k_{\nu'} r - \ell' \pi/2 \right) \right] \right]. \tag{3.11}
\]

Comparing coefficients of the \( \nu' \lambda' \ell' \mu' m' \) term for the incoming wave shows that

\[
\sum_{LM} B(\lambda\mu\ell mLM) C(\lambda\ell L|\mu' m'M) = \delta_{m', m} \delta_{\mu', \mu}. \tag{3.12}
\]

It will be recognized immediately from Eq. (3.6a) that
\[ B(\lambda \mu | \mu \lambda M) \equiv C(\lambda \mu | \mu \lambda M). \] (3.13)

Comparing coefficients of the outgoing wave, and using Eq. (3.13) gives
\[ S(\nu \lambda \mu \mu | \nu' \lambda' \lambda' \mu' \mu') \]
\[ = \sum_{LM} C(\lambda \mu | \mu \lambda M) \quad \sum_{LM} C(\lambda' \lambda' | \mu' \mu' M) \quad S_{LM}^{LM}(\nu \lambda \mu | \nu' \lambda' \lambda' \mu' \mu'). \] (3.14)

Because of the orthogonality relation in Eq. (3.6a), a corresponding equation can be written for the T-matrix,
\[ T(\nu \lambda \mu \mu | \nu' \lambda' \lambda' \mu' \mu') = \sum_{LM} C(\lambda \mu | \mu \lambda M) C(\lambda' \lambda' | \mu' \mu' M) \quad T_{LM}^{LM}(\nu \lambda \mu | \nu' \lambda' \lambda' \mu' \mu') \] (3.15)

where
\[ \sum T_{LM}^{LM} = 1 - S_{LM}^{LM}. \] (3.16)

It is convenient to carry the algebra a little further to get appropriate cross section formulas. From Eq. (2.23), the total cross section for the transition from state \( \nu \lambda \mu \) to \( \nu' \lambda' \mu' \) is
\[ \sigma(\nu \lambda \mu \rightarrow \nu' \lambda' \mu') = \pi k_{\nu}^{-2} \quad \sum_{LM} \sum_{\lambda \lambda'} \sum_{\mu \mu'} |T(\nu \lambda \mu \mu | \nu' \lambda' \lambda' \mu' \mu')|^{2}, \] (3.17)

which can be rewritten in terms of \( T_{LM}^{LM} \) as
\[ \sigma(\nu \lambda \mu \rightarrow \nu' \lambda' \mu') = \pi k_{\nu}^{-2} \quad \sum_{LM} \sum_{\lambda \lambda'} \sum_{\mu \mu'} \sum_{\mu \mu'} \]
\[ C(\lambda \mu | \mu \lambda M) \quad C(\lambda' \lambda' | \mu' \mu' M) \quad C(\lambda \mu | \mu \lambda M) \quad C(\lambda' \lambda' | \mu' \mu' M) \quad \]
\[ \times \quad T_{LM}^{LM}(\nu \lambda \mu | \nu' \lambda' \lambda') \quad T_{LM}^{LM}(\nu \lambda \mu | \nu' \lambda' \lambda') \] (3.18)
which is rather impractical. However, the magnetic quantum numbers
are usually unimportant experimentally, and can be eliminated. To get
the total cross section for the transition \( \nu \lambda \) to \( \nu' \lambda' \), irrespective of
\( \mu \) or \( \mu' \), one sums over all final states \( \mu' \), and averages over initial
states \( \mu \); i.e.,

\[
\sigma(\nu \lambda \rightarrow \nu' \lambda') = \frac{1}{2\lambda + 1} \sum_{\mu} \left[ \sum_{\mu'} \sigma(\nu \lambda \mu \rightarrow \nu' \lambda' \mu') \right]. \tag{3.19}
\]

When Eq. (3.18) is substituted into this expression, the orthogonality
relation in Eq. (3.6b) may be invoked twice and all the Clebsch-Gordon
coefficients eliminated, leaving finally the simple expression

\[
\sigma(\nu \lambda \rightarrow \nu' \lambda') = \frac{\pi}{(2\lambda + 1)k_\nu^2} \sum_{L} \sum_{M} |T^{LM}_{\nu \lambda \nu' \lambda'}|^2. \tag{3.20}
\]

Although it hasn't been shown, the U functions (and hence the S and T
matrices) in the coupled representation are independent of \( M \). Thus, the
sum over \( M \) above is just \( (2L + 1) \) times a single term.

\[
\sigma(\nu \lambda \rightarrow \nu' \lambda') = \frac{\pi}{(2\lambda + 1)k_\nu^2} \sum_{L} (2L + 1) |T^{L}_{\nu \lambda \nu' \lambda'}|^2. \tag{3.21}
\]

The coupled radial equations which actually determine the U functions
in the L,M basis are generated as before. That is, one starts with the
full Schrödinger equation, using Eqs. (3.9) and (3.7)

\[
\sum_{L'M'} C(\lambda L' L' M' | \mu M) \left[ H(\rho) - E \right] \\
\times \sum_{\nu' \lambda' L'} r^{-1} U_{\nu' \lambda' L' L' M'}(r) Y_{\nu' \lambda'}(r, \rho) R_{\nu' \lambda'}(\rho) = 0. \tag{3.22}
\]
This is then reduced by pre-multiplying by one of the expansion basis functions and then integrating over all coordinates except \(r\),

\[
C(\lambda \ell L | \mu \ell M) \sum_{\nu'} \int \int \int y_{\nu,\ell,\ell,LM}^*(r,\rho) R_{\nu,\ell,\ell}^*(\rho) \\
\times [H(r,\rho) - E] r^{-1} U_{\nu',\ell',\ell',LM}^*(r) y_{\nu',\ell',\ell'}(r,\rho) R_{\nu',\ell'}(\rho) \, d\rho \, dr = 0,
\]

(3.23)

where it has been recognized that \(L\) and \(M\) will be the same throughout the equation. Strictly speaking, the sum over \(\nu'\) and \(\lambda'\) must go over all hydrogen states (including continuum), and for any \(\lambda'\), there will be certain \(\ell'\) values to be summed, namely those which are consistent with triangle inequalities among \((\lambda',\ell',L)\). The close coupling approximation consists of only using a few basis states in the \(\nu',\lambda'\) sums.

In particular, the work in Chapters Two and Three uses only the 1s, 2s, and 2p states. For a given \(L\), this drastically limits the number of \(\ell'\) values. As a matter of fact, if one follows the coupled equations in Eq. (3.23) down to their explicit form, it will be found that for these hydrogen basis states, the maximum number of channels to be considered at any one time is four. (At first glance there would appear to be five, but parity requires that for functions to be coupled, the parity of \(\lambda' + \ell' - L\) must be the same, thus eliminating one.) Additionally, only a few of the lowest \(L\) set of equations are actually solved, when there are really an infinite number of them.
Spin Coupling and Exchange

A final point which should be discussed is that $H$ contains no spin terms. Consequently, the total spin operator $S$ commutes with $H$ and the spins of the electrons may be coupled to form spin eigenfunctions of $S^2$ and the $z$-component $S_z$ (quantum numbers $S$ and $M_z$). For two electrons, the spin coupling is trivial, and furthermore, the spin part factors from the spatial part of the full wavefunction. The modifications this induces in the previous treatment have no small effect, however. Consider Eq. (3.2). Functions which are to be eigenfunctions of spin and which also satisfy the Pauli principle may be constructed as

$$\psi_{\nu\mu\lambda}(\mathbf{r},\mathbf{p}) = \sum_{\ell m} 2\pi k \lambda^{-1/2} \frac{1}{\ell + 1} Y_{\ell m}(\hat{\mathbf{k}})$$

$$\times \left\{ \begin{array}{c}
\left[ \psi_{\nu\lambda\mu\ell m}(\mathbf{r},\mathbf{p}) + \psi_{\nu\lambda\mu\ell m}(\mathbf{p},\mathbf{r}) \right] (\alpha_1 \beta_2 - \beta_1 \alpha_2), \\
\left[ \psi_{\nu\lambda\mu\ell m}(\mathbf{r},\mathbf{p}) - \psi_{\nu\lambda\mu\ell m}(\mathbf{p},\mathbf{r}) \right] (\alpha_1 \beta_2 + \beta_2 \alpha_1).
\end{array} \right. \right\}^{\alpha_1 \alpha_2}$$

(3.24)

The coupled equations corresponding to this will be

$$\sum_{\nu',\lambda',\ell'} \left\{ \begin{array}{c}
Y_{\ell' \lambda' \lambda}\left( \mathbf{r}, \mathbf{p} \right) R^*_{\lambda' \lambda} \left( \mathbf{p} \right) \left[ H(\mathbf{r},\mathbf{p}) - E \right] \\
\times \left\{ \left[ \frac{1}{\nu' \lambda' \ell' \lambda \ell} \left( \mathbf{r}, \mathbf{p} \right) \right] \left( \mathbf{r}, \mathbf{p} \right) R_{\lambda' \lambda} \left( \mathbf{p} \right) \pm \left( \mathbf{r} \leftrightarrow \mathbf{p} \right) \right\} \right\} d\mathbf{p} d\mathbf{r} = 0 \quad (3.25)
$$

where the + and − signs are to be used for the singlet and triplet calculations respectively, and $(\mathbf{r} \leftrightarrow \mathbf{p})$ denotes the preceding term with $\mathbf{r}$ and $\mathbf{p}$ interchanged.
The complications here due to exchange are enormous. The above prescription still generates a differential equation on the $U$ functions from the first term in braces, but in the second term, the coordinates in $U$ are to be integrated over besides! Thus, the equations to be solved for $U$ are now a set of integro-differential equations. The general form of the equations will be

$$\left[ \frac{d^2}{dr^2} + k_v^2 - \frac{\ell(\ell + 1)}{r^2} \right] U_\gamma^\circ(r) = \sum_{\gamma'} U_{\gamma\gamma'}(r) U_{\gamma'}^\circ(r) \pm \sum_{\gamma'} \int K_{\gamma\gamma'}(r,r') U_{\gamma'}^\circ(r') dr', \quad (3.26)$$

where the collective index is $\gamma = (v\lambda \ell)$. This shows that $U_\gamma^\circ$ at $r$ depends not only on all other $U_{\gamma'}^\circ$ at $r$ and matrix elements of the potential $U_{\gamma\gamma'}$ at $r$, but also on itself and all other $U_{\gamma'}^\circ$ at all other values of the coordinate $r'$. The terms of the form

$$\int K_{\gamma\gamma'}(r,r') U_{\gamma'}^\circ(r') dr'$$

are called "non-local potentials", since they determine the behavior of $U_\gamma^\circ$ locally at $r$ in terms of its behavior in the entire domain.

Finally, allowance must be made in the total cross section formula for the existence of the singlet and triplet modes of scattering.

When the $+$ sign is chosen in Eq. (3.26), the cross section $\sigma^+$ calculated from Eq. (3.21) will be for the case of singlet pairing. When the $-$ sign is used, one will obtain the cross section $\sigma^-$ for triplet pairing. In an unpolarized system, the spin pairings are random, so these two possibilities must be averaged with the multiplicities $(2S + 1)$ as weighting factors; thus
\[
\sigma(\nu \lambda + \nu' \lambda') = \frac{1}{4} \left[ \sigma^+(\nu \lambda + \nu' \lambda') + 3 \sigma^-(\nu \lambda + \nu' \lambda') \right]. \tag{3.27}
\]

It is seen that the total transition \(\nu \lambda \rightarrow \nu' \lambda'\) can be decomposed into a sum of terms, each of which comes from a calculation for a particular \(L\) and \(S\); using Eqs. (3.21) and (3.27) allows one to write

\[
\sigma(\nu \lambda + \nu' \lambda') = \sum_{LS} Q^{LS}(\nu \lambda + \nu' \lambda'), \tag{3.28}
\]

where the partial cross sections are

\[
Q^{LS}(\nu \lambda + \nu' \lambda') = \frac{(2L + 1)(2S + 1)}{(2\lambda + 1)4k_{\nu}^2} \sum_{\lambda \lambda'} |T^{LS}(\nu \lambda \lambda'|\nu' \lambda' \lambda')|^2 \tag{3.29}
\]

With this equation, the Chapter comes to an end. The reader is now prepared for Chapter Two.
REFERENCES


CHAPTER TWO
CHAPTER TWO. CLOSE COUPLED CALCULATIONS OF ELECTRON-HYDROGEN ATOM SCATTERING USING A NONITERATIVE INTEGRAL EQUATION TECHNIQUE

This Chapter is composed of a manuscript which has been submitted recently to the Journal of Chemical Physics. In it, a noniterative integral equation approach to electron-hydrogen atom scattering, including exchange, has been developed for the case in which all available channels are open. The technique has been implemented on a computer for the calculation of cross sections in the 1s-2s strong coupling exchange approximation and the 1s-2s-2p close coupling exchange approximation. The results of these calculations were found to be in good agreement with those obtained by the iterative solution of the differential equations. The merits of the noniterative integral equation technique are compared with other computational schemes for obtaining scattering information.
1. THEORY

The integro-differential equations which describe the electron-hydrogen atom (EHA) system in the close coupling approximation\(^1\) present a number of problems for numerical computation. The most difficult of these to treat is the nonlocal potential which arises when the wave function is explicitly antisymmetrized in the two electron coordinates. The most obvious, and most common, technique employed to deal with this is a successive iteration scheme.\(^2,3,4,5,6\) Alternatively, the close coupled set of equations may be enlarged by additional equations, one for each exchange term, and the augmented set solved noniteratively.\(^7\)

When either method is used within the context of the differential equation formalism, the relevant numbers describing the scattering process are found by matching calculated wave functions to prescribed asymptotic forms. It is well known that this step may be eliminated by working with the equivalent integral equations.\(^8\) To date, this approach has not been extensively used, and until very recently, was implemented only with the iterative technique.\(^9\)

This paper presents an extension of the approach used by Sams and Kouri\(^10,11\) to generate for the EHA system a set of simple Volterra equations whose solutions may be easily calculated. As in the noniterative differential equation method, the number of equations is given by the number of channels plus the number of exchange terms. The developments reported here do not include a treatment of closed channels, but the extension to include closed channels is not viewed as a major
obstacle. The attractiveness of the present formulation is that the resulting equations are easy to program, and even such a simple integration algorithm as the repeated trapezoidal rule is found to give good results. Also, the desired result, the reactance matrix, is easily calculated from a set of integrals which are generated as part of the solution of the equations.

A second problem of the EHIA system is the long range multipole potential terms which are present when nonspherical hydrogen basis states are included in the expansion of the wave function. A special method has been developed to include the effects of such terms with a minimal effort. This method is discussed in detail in the following paper since it is not necessary for the basic development given here.

Partial Wave Analysis

The starting point for this report is the partial wave analysis in the coupled representation as given by Percival and Seaton. The scattering functions are coupled into sets which are simultaneous eigenfunctions of $L^2 = (\ell_1 + \ell_2)^2$ and $S^2 = (s_1 + s_2)^2$, where $\ell_1$, $\ell_2$, $s_1$, and $s_2$ are the orbital and spin momenta of electrons one and two. When the wavefunction is explicitly antisymmetrized in the two electron coordinates, the Hartree-Fock equations for the radial functions are
\[ \left[ \frac{d^2}{dR^2} - \frac{\lambda_2(\ell_2 + 1)}{R^2} + k_n^2 \right] F_L S(\nu \nu^0 | R) = \sum_{\mu} \left[ -\delta(\nu, \mu) 2R^{-1} + \sum_{\lambda} 2f_{\lambda}(\nu \mu; L) y_{\lambda}(\nu \mu | R) \right] F_L S(\mu \nu^0 | R) + \sum_{\mu} P(\mu | R) \sum_{\lambda} 2g_{\lambda}(\nu \mu; LS) \]

\[
\times \left[ R^\lambda \int_0^R r^{-\lambda-1} P(\nu | r) F_L S(\mu \nu^0 | r) dr - R^{-\lambda-1} \int_0^R r^\lambda P(\nu | r) F_L S(\mu \nu^0 | r) dr \right] \]

\[
+ \sum_{\mu} P(\mu | R) \sum_{\lambda} 2g_{\lambda}(\nu \mu; LS) \left[ \delta(\lambda, 0) \frac{1}{2} (E - E_\nu - E_\mu) \int_0^\infty P(\nu | r) F_L S(\mu \nu^0 | r) dr \right] \]

\[
- R^\lambda \int_0^\infty r^{-\lambda-1} P(\nu | r) F_L S(\mu \nu^0 | r) dr \right]. \quad (1)
\]

The quantities \( \nu \) and \( \mu \) are labels which represent the various sets of quantum numbers \( \{n, \ell_1, \ell_2\} \). The hydrogen atom state is specified by \( n \) and \( \ell_1 \), while the partial wave angular momentum of the incoming electron is specified by \( \ell_2 \). The numerical coefficients \( f_{\lambda}(\nu \mu; L) \) and \( g_{\lambda}(\nu \mu; LS) \) are related to the vector coupling coefficients. They are defined in the Appendix, as are the hydrogen radial functions \( P(\nu | R) \) and the integrals \( y_{\lambda}(\nu \mu | R) \). The Kronecker delta is denoted by \( \delta(\nu, \mu) \). Lengths are measured in units of \( a_0 \) (Bohr radius), and energies are measured in units of \( e^2/2a_0 \) (Rydbergs). The total energy \( E \) of the system, the channel wave number \( k_n \), and the atomic energy \( E_\nu \), for the specification \( \nu = \{n, \ell_1, \ell_2\} \), are related by

\[ E = E_\nu + k_n^2. \quad (2) \]

In the conventional definition of the energy axis, the value of zero is assigned to the atomic ground state energy. Thus, for scattering from
this state, the energy of the system is just the kinetic energy of the projectile. The radial function for the scattered electron which describes the transition of the system from state ν₀ to state ν is

\[ F_{LS}(νν₀|R). \]

In order to simplify Eq. (1), the following definitions are introduced:

the direct potential,

\[ V_L(νμ|R) \equiv -δ(ν,μ) \frac{2R^{-1}}{2} + \sum_λ 2f_λ(νμ;L) y_λ(νμ|R); \]  \hspace{1cm} (3)

the "exchange integrals",

\[ U_{LS}(νμλ;ν₀|R) \equiv \int_0^R r^{-λ-1} P(ν|r) F_{LS}(μν₀|r)dr, \]  \hspace{1cm} (4)

\[ Q_{LS}(νμλ;ν₀|R) \equiv \int_0^R r^λ P(ν|r) F_{LS}(μν₀|r)dr; \]  \hspace{1cm} (5)

and the constants,

\[ D_{LS}(νμλ;ν₀) \equiv 2g_λ(νμ;LS) \left[ a(νμλ) Q_{LS}(νμλ;ν₀) + U_{LS}(νμλ;ν₀) \right], \]  \hspace{1cm} (6)

where

\[ a(νμλ) \equiv δ(λ,0) \frac{1}{2} (E - E_ν - E_μ). \]  \hspace{1cm} (7)

A useful convention has been introduced in Eq. (6), namely,

\[ Q_{LS}(νμλ;ν₀) \equiv \lim_{R \to \infty} Q_{LS}(νμλ;ν₀|R). \]  \hspace{1cm} (8)
Whenever a function appears without explicit designation of its variable, its meaning is that implied by Eq. (8). A more compact expression for Eq. (1) is

\[
\left[ \frac{d^2}{dR^2} - \frac{\ell_2 (\ell_2 + 1)}{R^2} + k_n^2 \right] F_{LS}(\nu \nu^O|R) = W_{LS}(\nu \nu^O|R) + \sum_\mu \sum_\lambda P(\mu|R) R^\lambda D_{LS}(\nu \mu \lambda; \nu^O),
\]

(9)

where the combined direct and exchange potential is

\[
W_{LS}(\nu \nu^O|R) \equiv \sum_\mu V_L(\nu \mu|R) F_{LS}(\nu \nu^O|R) + \sum_\mu P(\mu|R) \sum_\lambda 2 \varepsilon_\lambda(\nu \mu;LS)
\times \left[ R^\lambda U_{LS}(\nu \mu \lambda; \nu^O|R) - R^{-\lambda-1} Q_{LS}(\nu \mu \lambda; \nu^O|R) \right].
\]

(10)

The radial functions which are solutions of Eq. (9) are completely defined for the scattering problem only when their asymptotic form is also specified. Since it is more convenient from a computational point of view to work with real functions, the required asymptotic form is taken to be

\[
F_{LS}(\nu \nu^O|R) \sim k_n^{-\frac{\ell_2}{2}}
\times \left[ \delta(\nu, \nu^O) \sin(k_n R - \ell_2 \pi/2) + R_{LS}(\nu \nu^O) \cos(k_n R - \ell_2 \pi/2) \right].
\]

(11)

This defines the elements of the reactance matrix (R matrix). Hereafter, the LS subscripts will be omitted with the understanding that these quantum numbers have already been specified for the problem at hand.
Noniterative Integral Equation Development

The condition in Eq. (11) may be most easily imposed on the radial functions by casting Eq. (9) into the equivalent integral equation

\[ F(\nu \nu^o | R) = \delta(\nu, \nu^o) F(\nu | R) + \int_0^\infty F(\nu | r_<) \ G(\nu | r_) \ W(\nu \nu^o | r) dr \]

\[ + \sum_{\mu} \sum_\lambda \left[ \int_0^\infty F(\nu | r_<) \ G(\mu | r_) \ P(\mu | r) \ r^\lambda dr \right] D(\nu \mu \lambda, \nu^o), \]  

(12)

where \( r_<, r_\) is the lesser (greater) of \( R \) and \( r \). The components of the Green function are

\[ F(\nu | r) = k_n^{1/2} r j(\ell_2 | k_n r), \]  

(13a)

\[ G(\nu | r) = - k_n^{1/2} r n(\ell_2 | k_n r), \]  

(13b)

where \( j(\lambda | r) \) and \( n(\lambda | r) \) are the spherical Bessel and Neumann functions, respectively, and the constants have been chosen to give a unit Wronskian.  

An extended form of the Sams-Kouri method is now developed for Eq. (12). First, the \( r_< \) and \( r_\) variables are eliminated to give

\[ F(\nu \nu^o | R) = F(\nu | R) \ C(\nu \nu^o) \]

\[ + G(\nu | R) \left[ A(\nu \nu^o | R) + \sum_{\mu'} \sum_{\lambda'} \delta(\nu, \nu') H_a(\nu' \mu' \lambda' | R) D(\nu' \mu' \lambda'; \nu^o) \right] \]

\[ - F(\nu | R) \left[ B(\nu \nu^o | R) + \sum_{\mu'} \sum_{\lambda'} \delta(\nu, \nu') H_b(\nu' \mu' \lambda' | R) D(\nu' \mu' \lambda'; \nu^o) \right], \]  

(14)
where
\begin{align}
A(\nu\nu^0|R) &\equiv \int_0^R F(\nu|r) \, W(\nu^0|R)dr, \quad (15) \\
B(\nu\nu^0|R) &\equiv \int_0^R G(\nu|r) \, W(\nu^0|R)dr, \quad (16) \\
H_a(\nu\nu\lambda|R) &\equiv \int_0^R F(\nu|r) \, P(\mu|r) r^\lambda dr, \quad (17) \\
H_b(\nu\nu\lambda|R) &\equiv \int_0^R G(\nu|r) \, P(\mu|r) r^{-\lambda-1}dr, \quad (18)
\end{align}

and
\begin{equation}
C(\nu\nu^0) = \delta(\nu,\nu^0) + B(\nu\nu^0) + \sum_\nu' \sum_\mu \sum_\lambda \delta(\nu,\nu') H_b(\nu'\mu'\lambda') D(\nu'\mu'\lambda';\nu^0). \quad (19)
\end{equation}

The convention in Eq. (8) has been used in Eq. (19). In its present form, Eq. (14) is not amenable to direct solution. An iterative technique must be used in order to handle the initially unknown C and D coefficients. The trick now is to generate an auxiliary set of equations from which these coefficients have been removed. The basis of the present development is the following ansatz for decomposing the radial functions:
\begin{align*}
F(\nu\nu^0|R) &= \sum_\nu F^0(\nu\nu'|R) \, C(\nu'\nu^0) \\
&\quad + \sum_\nu' \sum_\mu \sum_\lambda F^1(\nu;\nu'\mu'\lambda'|R) D(\nu'\mu'\lambda';\nu^0).
\end{align*} \quad (20)

It is not entirely obvious that the adoption of this form will allow defining equations to be written for the $F^0$ and $F^1$ which do not involve either the C or D coefficients. However, the following heuristic argument may be offered. The first summation has the effect of replacing
the C coefficients by a set of arbitrary functions $F^0$. The set of summations over $\nu', \mu', \lambda'$ may be understood by considering that one arbitrary function $F^1$ must be introduced to account for each exchange term $D$ which is to be eliminated.

Substituting Eq. (20) into the definitions of the $U$ and $Q$ integrals in Eqs. (4) and (5) leads to decompositions which are identical in form to that for $F$, viz.

\[
U(\nu\mu; \nu' | R) = \sum_{\nu'} U^0(\nu\mu; \nu' | R) C(\nu' \nu^0) \\
+ \sum_{\nu', \mu'} \sum_{\lambda'} U^1(\nu\mu; \nu' \mu' \lambda' | R) D(\nu' \mu' \lambda' ; \nu^0), \tag{21}
\]

\[
Q(\nu\mu; \nu' | R) = \sum_{\nu'} Q^0(\nu\mu; \nu' | R) C(\nu' \nu^0) \\
+ \sum_{\nu', \mu'} \sum_{\lambda'} Q^1(\nu\mu; \nu' \mu' \lambda' | R) D(\nu' \mu' \lambda' ; \nu^0), \tag{22}
\]

where

\[
U^0(\nu\mu; \nu' | R) = \int_0^R r^{-\lambda-1} P(\nu | r) F^0(\mu \nu' | r) dr, \tag{23}
\]

\[
U^1(\nu\mu; \nu' \mu' | R) = \int_0^R r^{-\lambda-1} P(\nu | r) F^1(\mu \nu' \mu' \lambda' | r) dr, \tag{24}
\]

and similarly for $Q^0$ and $Q^0$. Straightforward substitution will verify that the $W$, $A$, and $B$ functions can also be written in the form

\[
Z(\nu \nu^0 | R) = \sum_{\nu'} Z^0(\nu \nu' | R) C(\nu' \nu^0) \\
+ \sum_{\nu', \mu'} \sum_{\lambda'} Z^1(\nu \nu' \mu' \lambda' | R) D(\nu' \mu' \lambda' ; \nu^0), \tag{25}
\]
where the symbol \( Z \) can be replaced by \( W, A, \) or \( B, \) and the superscripted functions have the obvious definitions which follow from Eqs. (23) and (24).

Upon returning to Eq. (14), substituting the ansatz, and using Eq. (25) for \( A \) and \( B, \) there results the equation

\[
\sum_{\nu'} F^0(\nu\nu'|R) C(\nu'|\nu^0) + \sum_{\nu'} \sum_{\lambda'} F^1(\nu;\nu'\mu'\lambda'|R) D(\nu'\mu'\lambda';\nu^0) \\
= \sum_{\nu'} \left[ \delta(\nu,\nu') F(\nu'|R) + G(\nu|R) A^0(\nu\nu'|R) - F(\nu|R) B^0(\nu\nu'|R) \right] C(\nu'|\nu^0) \\
+ \sum_{\nu'} \sum_{\lambda'} \left[ \delta(\nu,\nu') H(\nu'\mu'\lambda'|R) + G(\nu|R) A^1(\nu;\nu'\mu'\lambda'|R) \\
- F(\nu|R) B^1(\nu;\nu'\mu'\lambda'|R) \right] D(\nu'\mu'\lambda';\nu^0)
\]

(26)

where

\[
H(\nu\mu\lambda|R) = G(\nu|R) H_a(\nu\mu\lambda|R) - F(\nu|R) H_b(\nu\mu\lambda|R).
\]

(27)

It is immediately evident that Eq. (26) may be satisfied identically by requiring that the arbitrary functions \( F^0 \) and \( F^1 \) satisfy the equations

\[
F^0(\nu\nu'|R) = \delta(\nu,\nu') F(\nu'|R) + G(\nu|R) A^0(\nu\nu'|R) - F(\nu|R) B^0(\nu\nu'|R),
\]

(28)

\[
F^1(\nu;\nu'\mu'\lambda'|R) = \delta(\nu,\nu') H(\nu'\mu'\lambda'|R) \\
+ G(\nu|R) A^1(\nu;\nu'\mu'\lambda'|R) - F(\nu|R) B^1(\nu;\nu'\mu'\lambda'|R).
\]

(29)
These are Volterra equations of the second kind whose numerical solutions present little difficulty. The methods used for their integration will be discussed in Section II.

Calculation Of The R Matrix

Now that the $F^0$ and $F^1$ functions have been defined, it must be determined how they are combined to yield the full radial scattering functions (i.e., how the $C$ and $D$ coefficients are calculated in terms of integrals over the $F^0$ and $F^1$ functions), and ultimately how the $R$ matrix can be computed. The definitions in Eq. (6) and (19) may be expanded by using the decompositions of the $Q$, $U$, and $B$ integrals to get

$$D(\nu \mu \lambda; \nu^0) = \sum_{\nu^1} \beta^0(\nu \mu \lambda; \nu^1) C(\nu^1 \nu^0)$$

$$+ \sum_{\nu^1} \sum_{\lambda^1} \beta^1(\nu \mu \lambda; \nu^1 \mu^1 \lambda^1) D(\nu^1 \mu^1 \lambda^1; \nu^0)$$

$$C(\nu \nu^0) = \delta(\nu, \nu^0) + \sum_{\nu^1} B^0(\nu \nu^1) C(\nu^1 \nu^0)$$

$$+ \sum_{\nu^1} \sum_{\lambda^1} \hat{B}(\nu; \nu^1 \mu^1 \lambda^1) D(\nu^1 \mu^1 \lambda^1; \nu^0)$$

where

$$\beta^0(\nu \mu \lambda; \nu^1) = 2g_{\lambda}(\nu \mu)[a(\nu \mu \lambda) Q^0(\nu \mu \lambda; \nu^1) - U^0(\nu \mu \lambda; \nu^1)]$$

(32)
\[ \beta^1(\nu \mu \lambda; \nu' \mu' \lambda') = 2 g^{1}_{\lambda}(\nu \mu) \left[ a(\nu \mu \lambda) \ Q^{1}(\nu \mu \lambda; \nu' \mu' \lambda') - \ U^{1}(\nu \mu \lambda; \nu' \mu' \lambda') \right] \]

(33)

and

\[ \hat{B}(\nu; \nu' \mu' \lambda') = B^{1}(\nu; \nu' \mu' \lambda') + \delta(\nu, \nu') \ H_{\mu}(\nu' \mu' \lambda'). \]

(34)

It will be convenient to introduce a "super" index set, defined by

\[ \zeta = \{\nu \mu \lambda\}, \quad \zeta' = \{\nu' \mu' \lambda'\}, \]

(35)

which is essentially a label for the exchange terms. With the aid of this abbreviation, Eqs. (30) and (31) may be written

\[ D(\zeta \nu^0) = \sum_{\nu'} \beta^0(\zeta \nu') \ C(\nu' \nu^0) + \sum_{\zeta'} \beta^1(\zeta \zeta') \ D(\zeta' \nu^0), \]

(36)

\[ C(\nu \nu^0) = \delta(\nu, \nu^0) + \sum_{\nu'} B^0(\nu \nu') \ C(\nu' \nu^0) + \sum_{\zeta'} \hat{B}(\nu \zeta') \ D(\zeta' \nu^0), \]

(37)

and the solution expressed in the matrix form

\[
\begin{pmatrix}
C \\
D
\end{pmatrix}
= \begin{pmatrix}
M^{-1} & -1 \\
0 & 0
\end{pmatrix},
\]

(38)

where the matrix \( M \) is defined by

\[
M = \begin{pmatrix}
B^0 - 1 & \hat{B} \\
\beta^0 & \beta^1 - 1
\end{pmatrix}.
\]

(39)
Let \( N_\nu \) be the number of channels and \( N_\zeta \) be the number of exchange terms. Then \( C \) is an \( N_\nu \times N_\nu \) matrix, \( D \) is an \( N_\zeta \times N_\nu \) matrix, and the unity in Eq. (38) is \( N_\nu \times N_\nu \). The matrix \( M \) is \( (N_\nu + N_\zeta) \times (N_\nu + N_\zeta) \).

The \( R \) matrix is identified from the asymptotic form of Eq. (12),

\[
F(\nu \nu^0 | R) \sim k_n^{-\frac{L_2}{2}} \{ \delta(\nu, \nu^0) \sin(k_n R - L_2 \pi/2) \\
+ \left[ -A(\nu \nu^0) - \sum \delta(\nu, \nu') \sum H_a(\nu' + \lambda') D(\nu' + \lambda'; \nu^0) \right] \\
\times \cos(k_n R - L_2 \pi/2) \} .
\]

Comparison of this expression with Eq. (11) yields

\[
R(\nu \nu^0) = -\sum_{\nu'} A^0(\nu \nu') C(\nu' \nu^0) - \sum_{\zeta'} \hat{A}(\nu \zeta') D(\zeta' \nu^0),
\]

where

\[
\hat{A}(\nu \zeta') \equiv \hat{A}(\nu + \nu' \lambda') = A^1(\nu + \nu' \lambda') + \delta(\nu, \nu') H_a(\nu + \mu' \lambda'),
\]

in analogy with Eq. (34). In matrix notation,

\[
R = -E \begin{bmatrix} C & \tilde{A}^0 \tilde{A} \end{bmatrix} = E \cdot M^{-1},
\]

where the \( N_\nu \times (N_\nu + N_\zeta) \) matrix \( E \) is

\[
E \approx \begin{bmatrix} A^0 & \hat{A} \end{bmatrix}
\]

It is thus a simple matter to evaluate the \( R \) matrix from the sets of \( A^i, U^i, A^i, \) and \( B^i \) integrals. In particular, only a single matrix inversion is required.
Finally, cross sections in the coupled representation for the various excitation processes are obtained from the equation

\[ Q_{LS}(n'l'_1 \rightarrow n'l_1) = \frac{(2L + 1)(2S + 1)}{4(2l'_1 + 1)\kappa_n} \sum_{\ell_2, \ell'_2} |T_{LS}(v'v)\rangle |^2, \tag{45} \]

where the sum is over the relevant partial waves and the T matrix is calculated from

\[ T_{LS} = -2R_{LS} \cdot (1 - iR_{LS})^{-1}. \tag{46} \]

It is possible to display in concise form the equations to be solved. For unity of presentation, a slight change in notation will be made, accompanied by the introduction of the label \( \xi \). The purpose of this is to eliminate the artificial distinction between those quantities bearing 0 or 1 superscripts. The rules governing \( \xi \) are given here:

1. for \( \xi' = v' \),

\[ F_{\xi'}, (v | R) \equiv F^0(v'v' | R), \]

\[ U_{\xi'}, (v\mu\lambda | R) \equiv U^0(v\mu\lambda; v' | R), \text{ etc.}; \tag{47} \]

2. for \( \xi' = \xi' \),

\[ F_{\xi'}, (v | R) \equiv F^1(v; v'\mu'\lambda' | R), \]

\[ U_{\xi'}, (v\mu\lambda | R) \equiv U^1(v\mu\lambda; v'v'\lambda' | R), \text{ etc.}. \tag{48} \]
The inhomogeneities in Eqs. (28) and (29) are handled by the convention

\[
\phi_{\xi'}(\nu|R) = \begin{cases} 
\delta(\nu,\nu') F(\nu'|R), & \xi' = \nu', \\
\delta(\nu,\nu') H(\nu'\mu'\lambda'|R), & \xi' = \xi'.
\end{cases}
\]  

(49)

Evidently there are \( N = N_\nu + N_\xi \) different values of \( \xi \). For any particular \( \xi' \), there will be a set of coupled equations which define \( N \) functions.

These are

\[
F_{\xi'}(\nu|R) = \phi_{\xi'}(\nu|R) + G(\nu|R) A_{\xi'}(\nu|R) - F(\nu|R) B_{\xi'}(\nu|R),
\]

\[1 \leq \nu \leq N_\nu,\]  

(50)

\[
X_{\xi'}(\nu\mu\lambda|R) = U_{\xi'}(\nu\mu\lambda|R) - R^{-2\lambda-1} Q_{\xi'}(\nu\mu\lambda|R),
\]

\[1 \leq \xi \leq N_\xi,\]  

(51)

where

\[
\begin{aligned}
\left\{ A_{\xi'}(\nu|R) \right\} &= \int_o^R \left\{ F(\nu'|r) \right\} \left[ \sum_{\nu'} V(\nu\nu'|r) F_{\xi'}(\nu'|r) \\
&+ \sum_{\nu',\mu'} \delta(\nu,\nu') 2g_{\lambda'}(\nu'\mu'|r) P(\mu'|r) r^{\lambda'} X_{\xi'}(\nu'\mu'\lambda'|r) dr \right],
\end{aligned}
\]

(52)

and

\[
\begin{aligned}
\left\{ U_{\xi'}(\nu\mu\lambda|R) \right\} &= \int_o^R \left\{ r^{-\lambda-1} \right\} P(\nu|r) F_{\xi'}(\nu|r) dr, \\
\left\{ Q_{\xi'}(\nu\mu\lambda|R) \right\} &= \int_o^R \left\{ r^\lambda \right\} \end{aligned}
\]

(53)
By judicious use of a Kronecker delta in Eq. (51), these equations may be written in the matrix form

\[
\begin{align*}
\begin{bmatrix}
F(R) \\
\varphi(R) \\
X(R)
\end{bmatrix}
&= 
\begin{bmatrix}
R \\
0 \\
0
\end{bmatrix}
+ 
\int_0^R 
\begin{bmatrix}
C_1(R,r) & C_2(R,r) \\
C_3(R,r) & 0
\end{bmatrix}
\begin{bmatrix}
F(r) \\
\varphi(r) \\
x(r)
\end{bmatrix} 
\, dr,
\end{align*}
\]

which displays somewhat "pictorially" the nature of the present formulation. In this construction, columns are indexed by \( \xi' \), rows by \( \nu \) and \( \xi \). Let no confusion exist concerning the definition of the \( N_\nu \times N_\nu \) matrix \( F_\nu \). Although the true radial scattering functions were denoted by this symbol, they are not needed after the \( R \) matrix has been identified, and \( F \) now stands for the solutions of Eqs. (28) and (29).

The kernels \( C_\nu(R,r) \) are not hard to derive, and are given here for the sake of completeness. They are

\[
G_1(\nu\nu'|R,r) = \left[ G(\nu|R) \ F(\nu|r) - F(\nu|R) \ G(\nu|r) \right] \ V(\nu\nu'|r),
\]

\[
G_2(\nu;\nu'\mu'\lambda'|R,r) = \left[ G(\nu|R) \ F(\nu'|r) - F(\nu|R) \ G(\nu|r) \right] 
\times \delta(\nu,\nu') \ 2g_\lambda(\nu'\mu') \ P(\mu'|r) \ r^{\lambda'},
\]

\[
G_3(\nu\mu;\mu'|R,r) = \left[ r^{\lambda-1} - R^{-2\lambda-1} \ r^{\lambda} \right] P(\nu|r) \ \delta(\mu,\mu').
\]

Finally, it is seen that the full set of radial scattering functions, in matrix form, may be found from the upper left \( N_\nu \times N_\nu \) functions in the product matrix.
This concludes the formal developments of this paper. In the next section, attention will be directed to details of the computations, while Section III will discuss the results which were obtained.

2. COMPUTATIONAL ASPECTS

The calculations to be presented in the next section were based on Eqs. (50) - (53). A detailed discussion of the mechanics of integration of these equations may be found elsewhere. However, a brief description based on Eqs. (54) and (55) may be given as follows. It will be noted that

\[ G_i(R, R) = 0, \quad i = 1, 2, 3. \]  

(56)

The implication of this is clear; the submatrices \( F(R) \) and \( X(R) \) depend only on their values at coordinates \( r \) which are strictly less than \( R \). The numerical integration of Eq. (54) is performed by replacing the continuous variable \( R \) by a set of quadrature points \( \{R_i\} \), and replacing the integrals by quadrature sums. Given the functions \( F(R_i) \) and \( X(R_i) \), the solution at \( R_{i+1} \) is constructed in two steps. First, \( F(R_i) \) and \( X(R_i) \) are used to calculate \( F(R_{i+1}) \). Second, \( F(R_i) \) is used to calculate \( X(R_{i+1}) \). Hence, the solution matrix is easily stepped out from the origin once the starting value is known. The required initial condition is

\[ F(0) = 0, \quad X(0) = 0. \]  

(57)
A program was written to perform these calculations in double precision on an IBM 7094 computer. All timings reported in the next section are based on this program run on this computer. It requires specification of E, L, S, parity, and a list of hydrogen basis states, from which the possible scattering channels and necessary numerical coefficients are constructed. For flexibility and efficiency, the range of integration is divided into two regions, the inner region where the potential is stronger being given a smaller step size than that used in the outer region. Six parameters governing the integration are required—step size and number of steps for each region, and two cutoff values. The cutoff parameters are values of R chosen so that the contributions from the exponentially decaying terms

\[ P(\mu|R) R^\lambda \]

in Eq. (52) and

\[ e^{-\alpha R} p(\alpha R) \]

in Eq. (A10) are of negligible magnitude.

By integrating all columns of F and X simultaneously, it is a simple matter to interrupt the integration at any point and compute the R matrix and cross sections. Thus, for each calculation, it is possible to examine convergence of the results with respect to the range of integration. It should be noted that for large multichannel calculations, the solutions for each \( \xi \) may be calculated independently and the resulting columns of A, B, and \( \beta \) integrals saved in peripheral storage. After all \( N \) calculations have been performed, the matrix \( M \) may be constructed, inverted, and combined with \( E \) to yield \( R \). Such an approach
requires less core storage but is obviously less efficient since the same \( P \), \( F \), and \( G \) functions must be computed \( N \) times. This procedure was not used for any of the calculations in this paper.

All integrals in the present work are evaluated by application of the repeated trapezoidal rule, the principal advantages of which are simplicity of programming and minimal storage requirements. The criterion used to define convergence of this scheme with respect to step size is that elements of the \( R \) matrix change by only a few parts in \( 10^4 \) as the step size is halved.

Noteworthy of the present method is the fact that calculated \( R \) matrices are always symmetric to better than one part in \( 10^9 \). In the case of three and four channel calculations in which nonspherical hydrogenic states are present, the very long range \( R^{-2} \) and \( R^{-3} \) terms in \( V(R) \) are treated by the method described in the following paper. The "exact" integration of the equations is carried out to a point \( R_N \), yielding a perfectly symmetric \( R \) matrix. The values of the \( A \) and \( B \) integrals are then projected to infinity and the \( R \) matrix again calculated. This final matrix, from which the cross sections tabulated here are computed, is always symmetric to within 1\% and often to within 0.1\%.

3. NUMERICAL RESULTS AND DISCUSSION

In this section, partial wave cross sections which have been calculated by the present method are presented. These numbers are generally as sensitive to the quality of calculation as are the \( R \) matrix elements, and it is felt that their tabulation should provide a compact and adequate
demonstration of the results obtainable. Both convergence studies and extensive tabulations of $R$ matrices and cross sections, giving comparison with previously published results, are available elsewhere.$^{13}$

The calculations fall into three categories according to complexity—ls single channel, ls-2s strong coupling, and ls-2s-2p close coupling. Each of these will be discussed in the following paragraphs. It is not the purpose of this paper to predict new values of cross sections for comparison with extant experimental results. Indeed, nearly every calculation verifies the results found in previously published work. The discussions, therefore, deal primarily with a few of the details of the integration and general observations and comments concerning the agreement of past and present results. Recall that lengths are in units of $a_0$ and energies are in units of Rydbergs.

Single Channel Phase Shifts

When the hydrogen atom is described by just a ls state, there is only one channel for each L value, namely, $\nu = \{1,0,L\}$. The $R$ matrix reduces to a single number, $R_{LS}$, and the phase shift (excluding an additive multiple of $\pi$) is calculated from

$$\delta_{LS} = \tan^{-1} R_{LS}.$$ 

Single channel calculations were performed primarily for the purpose of testing the integration algorithm. Since these results are of limited utility, they are not tabulated here. Various entries in the table of Sams and Kouri$^{10}$ were checked, together with several of the results
collected in Table II of the review article by Burke and Smith. Results converged to five decimals require a step size of 0.01 and range of 15 for singlet calculations, and take 20 seconds to calculate. It may be noted that convergence to better than 1% can be obtained with a step size of 0.1 and requires about 2½ seconds.

1s-2s Strong Coupling Calculations

The first multichannel calculations performed with the present method were of the "strong coupling" type, in which the hydrogen atom is described by a combination of 1s and 2s states. There are four exchange terms in these calculations, giving rise to six sets of coupled equations. Convergence studies at a number of E, L, and S values led to the adoption of the following integration algorithm. An inner region is defined from 0 to 10, through which the equations are integrated with a 0.025 step. Integration is continued from 10 to 30 using a 0.050 step. Precision in the cross sections is within two parts in $10^4$. The exchange terms were retained throughout the 0 to 30 range. This algorithm, which requires 42-44 seconds, was used for both Tables I and II.

Strong coupling calculations have been previously performed by Marriott and Smith. Marriott, using the noniterative differential equation technique, calculated only $L = 0$ cross sections while Smith, using the iterative approach, carried out calculations for $L = 0, 1, \text{and } 2$. In Table I there is a comparison of the results of the present work with those of both Marriott and Smith for $L = 0$. In general, the present
calculations are in better agreement with Marriott, with only three
exceptions—triplet \( Q(1s-2s) \) at \( E = 0.81 \) and \( E = 2.25 \), and triplet
\( Q(1s-1s) \) at \( E = 2.25 \).

The direct and excitation cross sections for \( L \leq 2 \) are contained
in Table II. Values shown for comparison are those of Smith\(^2\), where
available. These are supplemented by the results of Marriott\(^7\) (given
by Smith) and of Burke and Smith.\(^6\) Agreement is quite good with few
exceptions. In nearly every instance for which there is discrepancy
greater than 1%, reference to Smith's estimate of reliability for those
particular results shows them to be of poorer quality than the others.
His estimate is the magnitude of the error in the reciprocity relation

\[
\epsilon = \left| k_{1s}^2 Q(1s-2s) - k_{2s}^2 Q(2s-1s) \right|. 
\]

A necessary, but not sufficient, condition for the exact results is that
\( \epsilon = 0 \). In the case of Smith's \( L = 1 \) singlet cross sections at \( E = 0.81 \),
the error was \( \epsilon = 0.025 \), while the value of \( Q(1s-2s) \) itself was only
0.008. The present results, on the other hand, reflect a symmetry of
nine significant digits. It is not surprising, therefore, that these
two sets of results are in bad agreement. Similar remarks hold for the \( Q(1s-2s) \)
triplet results at \( E = 1.0 \) for both \( L = 0 \) and \( L = 2 \). In general, however,
where Smith's results are "good" by his standard, significant agreement
is evident.
1s-2s-2p Close Coupling Calculations

The inclusion of the 2p state in the hydrogen basis contributes one more channel to the calculation when \( L = 0 \), and two more channels when \( L > 0 \). A greater number of angular momentum couplings are now possible as well, giving rise to many more exchange terms. For \( L = 0 \), the number of exchange terms is 10, which means that a total of 13 sets of coupled equations need to be integrated. For \( L = 1 \), there are 17 exchange terms and a total of 21 sets of coupled equations. For any \( L \geq 2 \), the complexity of the calculation is at a maximum: 18 exchange terms and 22 sets of coupled equations.

Not only does the inclusion of the nonspherical 2p state greatly increase the size of these calculations, but it also complicates convergence of the integration with respect to range. This is because the potential no longer decays exponentially, but contains much longer range \( R^{-2} \) and \( R^{-3} \) terms. If the integration is arbitrarily stopped, at 40 say, and cross sections calculated without accounting for this long range behavior, results can be in error by as much as 50\%, particularly in \( Q(2s-2s) \). In the following paper, a technique formally resembling a Born approximation is presented which allows the exact integration to be stopped at a point \( R_N \), and the values of the integrals then projected from \( R_N \) to infinity. The transformation which is actually used consists of the first two terms of an infinite series. The error incurred by this truncation is proportional to \( R_N^{-2} \) at worst, and probably represents the major source of uncertainty in the final results.
In order to assess the reliability of the results of the projection procedure, two types of observations are made: the convergence of final results with respect to increasing $R_N$, and the symmetry of the final $R$ matrix. The equations are first integrated exactly through an inner region, from zero to 40. An outer region is then defined from 40 to 200. At $R_N = 40$, the integration is temporarily interrupted and the current values of the integrals used to calculate an $R$ matrix and cross sections. This reactance matrix is denoted by $R_N$. Values of the A and B integrals are then corrected for the long range potential and used to calculate a "projected $R$ matrix", denoted simply by $R$, together with cross sections. The exact integration is then resumed, with this procedure being repeated at $R_N = 80, 120, 160$, and 200. In this way it is possible to observe convergence with respect to increasing $R_N$ of both the exact $R_N$ and the projected $R$.

In order to use the degree of symmetry of $R$ as a test of quality, it is necessary to have a well-defined measure of this property. The asymmetry of the matrix, parameterized as

$$\alpha = \max |[R(\nu\nu') - R(\nu'\nu)])/R(\nu\nu')|,$$

seems to be a useful characterization. It gives an estimate of how well the "perfect" symmetry found in $R_N$ is retained in the calculation of $R$. It is expected to tend toward zero as $R_N$ is increased. This is because the calculation of the transformation becomes more accurate and also because there is less potential for which correction is being made.

Generally, changes in individual elements of $R$ as $R_N$ increased from 160 to 200 were always less than 8 parts in 10, while asymmetries
were always less than 0.005. For the majority of calculations, however, elements of $R$ actually changed less than one part in $10^4$, with asymmetries less than 0.00005.

A few calculations on both three and four channel problems testing convergence with respect to step size showed that integration from the origin to 40 with a 0.025 step size gave cross section values to within five parts in $10^4$. For integration beyond 40, a step size of 0.250 proved adequate to maintain precision within five parts in $10^6$. The exponentials in both the direct and exchange potentials were retained to 40.

Total execution times for this algorithm are 6 minutes for $L = 0$, 13.8 minutes for $L = 1$, 15.5 minutes for $L = 2$, and 16.4 minutes for $L = 3$. Approximately 10% of the total execution time is used for the integration through the outer region. The projection requires 2 to 5 seconds.

Cross sections calculated in the 1s-2s-2p exchange approximation are given in Tables III – VI. Omissions in the tables are simply calculations which were not done. For comparison, the partial wave cross sections obtained by Burke, Schey, and Smith (BSS), using an iterative differential equation technique, are also shown. In general, the two sets of results are in very good agreement. There are two particular cases, however, which need discussion. These are the $L = 0$ results at $E = 2.25$, and the $L = 3$ singlet case for $E = 0.81$.

The three channel calculations at $E = 2.25$ yield cross sections which differ completely from the BSS results. The source of such disagreement is unknown. The fault does not seem to lie in the projection
procedure. As \( R_N \) was increased from 160 to 200, changes in the elements of \( R \) were less than 1.5 parts in \( 10^4 \). Furthermore, the asymmetry parameter was only 0.00015. When additional calculations on the singlet state were done to examine step size convergence, anomalous behavior was observed. Halving the step size from 0.050 to 0.025 changed results by less than 3%, while halving it again to 0.0125 effected changes on the order of 10%.

It has been observed in other recent work with the noniterative integral equation method that occasional situations arise in which the solution vectors fail to maintain their linear independence, and this when all channels are open. The remedy employed was a triangularization procedure which forced linear dependence. This may be the explanation of the difficulty here.

The present results are also suspect on purely physical grounds. Individual cross sections are expected to be relatively smooth functions of the energy (when closed channel resonances are excluded). With respect to the energy behavior suggested by the other \( L = 0 \) results, which agree well with BSS values, the \( 1s-2s \) and \( 1s-2p \) cross sections at \( E = 2.25 \) seem quite erroneous, with order of magnitude discrepancies.

Concerning the \( L = 3 \) singlet results at \( E = 0.81 \), it should be noted that the BSS iterative method failed to converge for this calculation. It was found that results for scattering in this state could not be obtained by the noniterative integral equation technique either. The present manifestation of difficulty was that before the equations had been integrated to 40, the values of all of the A and B integrals
(and perhaps the U and Q integrals as well) had exceeded the maximum number allowable in the IBM 7094. The cause of this behavior has not been determined. A possible solution is scaling of the equations.

Certain indications of incipient trouble were noted in the \( L = 1 \) and \( L = 2 \) singlet calculations at this energy. It had been observed that for most calculations, the values of the A and B integrals ranged over four powers of ten (\( 10^{-2} \) to \( 10^{+1} \)), and over two powers of ten for a given \( \xi \). However, for the \( L = 1 \) calculation just mentioned, integral values ranged over 6 powers of ten, and for a given \( \xi \), over 4 powers. For \( L = 2 \), integral values ranged over 7 powers of ten, and over 5 powers for a given \( \xi \). There is apparently some numerical difficulty in obtaining these results; a greater discrepancy than usual can be seen in the tables for these cases as well.

4. SUMMARY AND CONCLUSIONS

A noniterative integral equation method has been applied to electron scattering from atomic hydrogen within the context of the close coupled exchange approximation. Two channel calculations with a \( 1s-2s \) basis were carried out for \( L = 0, 1, \) and \( 2 \), and three and four channel calculations with a \( 1s-2s-2p \) basis were carried out for \( L = 0, 1, 2, \) and \( 3 \). The results of this work have implications for both the problem and the method.

Regarding the problem itself, it may be said that the present results provide substantial verification by an entirely independent
method of previous calculations. In most cases, agreement is within 1%. Random disagreements larger than this are scattered in the tables with no discernible pattern. The only exception to this is for \( E = 0.81 \), where several discrepancies greater than 1% can be found in the four channel calculations. Noteworthy is the persistent failure to obtain results for the \( L = 3 \) singlet state at this energy.

The method appears generally capable of treating efficiently and accurately scattering systems in which account is taken of electron exchange. Iteration is avoided by generating additional equations to be solved; however, the required solutions can be constructed so rapidly that this is not a disadvantage. We have noted a few cases in which accurate results were not obtained, in particular the three channel calculations at \( E = 2.25 \). This is not viewed as a serious problem since similar difficulties were encountered\(^{17} \) and overcome in obtaining scattering information for atom-diatom collisions leading to rotational or vibrational excitation. In these cases it has been possible to obtain accurate results by judiciously scaling the inhomogeneous part of the Volterra equations and by applying stabilization transformations in order to insure that as the solutions are propagated they maintain their linear independence. For this reason we are optimistic that these procedures can also be used to insure the accuracy of the noniterative integral equation approach to the EHA system.
APPENDIX

In order to carry out a partial wave analysis of the compound system electron plus hydrogen atom, it is necessary to have the eigenfunctions and energies of the atomic system. Let \( H(r) \) be the Hamiltonian (in atomic units) for the hydrogen atom. Then

\[
H(r) \psi(n\lambda m| r) = E_n \psi(n\lambda m| r)
\]

(A1)

where

\[
E_n = -\frac{1}{n^2} \text{ Rydbergs}
\]

(A2)

Assigning the zero of energy to the ground state gives

\[
E_n = 1 + E_n.
\]

(A3)

The hydrogen wavefunctions are

\[
\psi(n\lambda m| r) = r^{-1} P_{n\lambda}(r) Y_{\lambda m}(\hat{r})
\]

(A4)

where \( r = | r | \) and \( \hat{r} = r/r \) is shorthand notation for the angles \( \theta \) and \( \phi \). The \( Y_{\lambda m}(r) \) are the angular momentum eigenfunctions; the \( P_{n\lambda}(r) \) are the radial functions which satisfy the orthonormality relation

\[
\int_0^{\infty} P_{n\lambda}(r) P_{n'\lambda}(r) dr = \delta_{n,n}'.
\]

(A5)

Explicit formulae for \( r^{-1} P_{n\lambda}(r) = R_{n\lambda}(r) \) may be found in Pauling and Wilson. 18

In the partial wave analysis, the angular and spin functions for the two electrons are coupled into eigenfunctions of \( L^2 = (L_1 + L_2)^2 \) and \( S^2 = (S_1 + S_2)^2 \). In the course of reducing the Hartree-Fock equations
for the system, there arise matrix elements of the Legendre polynomial $P_\lambda(\hat{r}_1, \hat{r}_2)$ between states in this coupled representation. These are

$$f_\lambda(\ell_1, \ell_2, \ell_1', \ell_2'; L) = \langle \ell_1 \ell_2 L | P_\lambda | \ell_1' \ell_2' L \rangle$$  \hspace{1cm} (A6)

$$g_\lambda(\ell_1, \ell_2, \ell_1', \ell_2'; L) = (-1)^{\ell_1 + \ell_2 - L} \langle \ell_1 \ell_2 L | P_\lambda | \ell_2' \ell_1' L \rangle$$  \hspace{1cm} (A7)

They may be evaluated by using the equations of Edmonds\textsuperscript{19} on pp. 50, 99, and 114. In the notation of this article

$$f_\lambda(\nu \nu'; L) = f_\lambda(\ell_1 \ell_2, \ell_1' \ell_2'; L)$$  \hspace{1cm} (A8a)

$$g_\lambda(\nu \nu'; LS) = (-1)^{1-S} g_\lambda(\ell_1 \ell_2, \ell_1' \ell_2'; L)$$  \hspace{1cm} (A8b)

when the factor $(-1)^{1-S}$ has been inserted to take care of the necessary symmetrization or antisymmetrization of the spatial wavefunction. It is important that these coefficients do not couple states for which $(\ell_1 + \ell_2 - L)$ and $(\ell_1' + \ell_2' - L)$ are of different parity.

The radial function $y_\lambda$ is defined by

$$y_\lambda(n\ell_1, n'\ell_1'; R) = R^{-\lambda-1} \int_0^R r^\lambda p_{n\ell_1}(r) P_{n'\ell_1'}(r) dr$$

$$+ R^{\lambda} \int_R^\infty r^{-\lambda-1} P_{n\ell_1}(r) P_{n'\ell_1'}(r) dr .$$  \hspace{1cm} (A9)

When this expression is explicitly evaluated, it can be written in the form

$$R y_\lambda(\nu \nu'; R) = (\alpha R)^{-\lambda} \tau_\lambda(\nu \nu') + e^{-\alpha R} p(\alpha R)$$  \hspace{1cm} (A10)

where $\tau$ is a constant, $p$ is a finite polynomial, and $\alpha = (n + n')/nn'$. 
REFERENCES


12 A. Messiah. Quantum Mechanics (North-Holland Publ. Co., Amsterdam, 1968) Vol. I. The definitions of $j(k|\rho)$ and $n(k|\rho)$ used in the present paper are the ones of this reference.

13 Dwayne L. Knirk, thesis.
Recent work on other problems using the noniterative integral equation approach has shown that the use of Simpson's rule allows step sizes to be increased by a factor of 5-10 while maintaining the same precision with very little added effort. See D. J. Kouri and E. F. Hayes, J. Chem. Phys. 54, 878 (1971).

Extensive tabulations of $R_N$ and $R$ matrices at each $R_N$, together with $\alpha$ values, can be found in Ref. 13.


TABLE I

Comparison of $L = 0$ cross sections (in units of $\pi a_0^2$) in the $1s-2s$ "strong coupling" exchange approximation. For a given energy, first row entries are results from the present work, while second row entries are results from Marriott (Ref. 7). Except where noted, third row entries are from Smith (Ref. 2). Numbers in parentheses give the power of ten by which the preceding entry must be multiplied.

<table>
<thead>
<tr>
<th>E</th>
<th>Q($1s-1s$) singlet</th>
<th>Q($1s-1s$) triplet</th>
<th>Q($1s-2s$) singlet</th>
<th>Q($1s-2s$) triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>0.4311 (0)</td>
<td>0.36830 (1)</td>
<td>0.3815 (-1)</td>
<td>0.1905 (-1)</td>
</tr>
<tr>
<td></td>
<td>0.4309 (0)</td>
<td>0.36832 (1)</td>
<td>0.383 (-1)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.4358 (0)</td>
<td>0.36873 (1)</td>
<td>0.384 (-1)</td>
<td>0.0</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2826 (0)</td>
<td>0.29029 (1)</td>
<td>0.7212 (-1)</td>
<td>0.2182 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.2828 (0)</td>
<td>0.29030 (1)</td>
<td>0.72 (-1)</td>
<td>0.21 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.2856 (0)</td>
<td>0.28954 (1)</td>
<td>0.714 (-1)</td>
<td>0.27 (-2)</td>
</tr>
<tr>
<td>1.44</td>
<td>0.1396 (0)</td>
<td>0.18295 (1)</td>
<td>0.5472 (-1)</td>
<td>0.6109 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.1397 (0)</td>
<td>0.18294 (1)</td>
<td>0.547 (-1)</td>
<td>0.61 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.140 (0)(^a)</td>
<td>0.1829 (1)(^a)</td>
<td>0.547 (-1)(^a)</td>
<td>0.61 (-2)(^a)</td>
</tr>
<tr>
<td>2.25</td>
<td>0.9028 (-1)</td>
<td>0.9701 (0)</td>
<td>0.2401 (-1)</td>
<td>0.6742 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.904 (-1)</td>
<td>0.9714 (0)</td>
<td>0.242 (-1)</td>
<td>0.73 (-2)</td>
</tr>
<tr>
<td></td>
<td>0.88 (-1)</td>
<td>0.971 (0)(^a)</td>
<td>0.238 (-1)</td>
<td>0.73 (-2)(^a)</td>
</tr>
</tbody>
</table>

\(^a\) These values are taken from Reference 6.
TABLE II

Elastic and excitation cross sections (in units of πa₀²) in the ls–2s strong coupling exchange approximation. Rows are labelled by "s" for singlet and at "t" for triplet results. Numbers in parentheses give the power of ten by which the preceding entry must be multiplied. Except where otherwise noted, the results of Smith (Ref. 2) are shown below each entry for comparison.

<table>
<thead>
<tr>
<th>E</th>
<th>L</th>
<th>0</th>
<th>Q(1s–1s)</th>
<th>2</th>
<th>0</th>
<th>Q(1s–2s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
<td></td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>----------</td>
<td>-----</td>
<td>-----</td>
<td>----------</td>
</tr>
<tr>
<td>0.81</td>
<td>s</td>
<td>0.4311 (0)</td>
<td>0.3882 (-1)</td>
<td>0.1627 (-2)</td>
<td>0.3815 (-1)</td>
<td>0.1735 (-2)</td>
</tr>
<tr>
<td></td>
<td>.4358 (0)</td>
<td>.46 (-1)</td>
<td>---</td>
<td>.384 (-1)</td>
<td>.8 (-2)</td>
<td>---</td>
</tr>
<tr>
<td>t</td>
<td>0.36830(+1)</td>
<td>0.13874(+1)</td>
<td>0.4630 (-1)</td>
<td>0.3954 (-3)</td>
<td>0.1676 (0)</td>
<td>0.5802 (-2)</td>
</tr>
<tr>
<td></td>
<td>.3687 (+1)</td>
<td>.13768(+1)</td>
<td>---</td>
<td>.0</td>
<td></td>
<td>.1736 (0)</td>
</tr>
<tr>
<td>1.00</td>
<td>s</td>
<td>0.2826 (0)</td>
<td>0.3383 (-1)</td>
<td>0.1453 (-2)</td>
<td>0.7212 (-1)</td>
<td>0.5764 (-1)</td>
</tr>
<tr>
<td></td>
<td>.2856 (0)</td>
<td>.333 (-1)</td>
<td>.14 (-2)</td>
<td>.714 (-1)</td>
<td>.51 (-1)</td>
<td>.0</td>
</tr>
<tr>
<td>t</td>
<td>0.29029(+1)</td>
<td>0.11618(+1)</td>
<td>0.5782 (-1)</td>
<td>0.2182 (-2)</td>
<td>0.1522 (0)</td>
<td>0.4352 (-1)</td>
</tr>
<tr>
<td></td>
<td>.28954(+1)</td>
<td>.1157 (+1)</td>
<td>.57 (-1)</td>
<td>.27 (-2)</td>
<td>.161 (0)</td>
<td>.46 (-1)</td>
</tr>
<tr>
<td>1.44</td>
<td>s</td>
<td>0.1396 (0) b</td>
<td>0.1114 (-1)</td>
<td>0.6433 (-3)</td>
<td>0.5472 (-1)</td>
<td>0.5331 (-1)</td>
</tr>
<tr>
<td></td>
<td>.1397 (0) b</td>
<td>.107 (-1)</td>
<td>.5 (-3)</td>
<td>.547 (-1) b</td>
<td>.53 (-1)</td>
<td>.53 (-2)</td>
</tr>
<tr>
<td>t</td>
<td>0.18295(+1) b</td>
<td>0.8083 (0)</td>
<td>0.6951 (-1)</td>
<td>0.6109 (-2)</td>
<td>0.7360 (-1)</td>
<td>0.5724 (-1)</td>
</tr>
<tr>
<td></td>
<td>.18294(+1) b</td>
<td>.815 (0)</td>
<td>.68 (-1)</td>
<td>.61 (-2) b</td>
<td>.735 (-1)</td>
<td>.577 (-1)</td>
</tr>
<tr>
<td>2.25</td>
<td>s</td>
<td>0.9028 (-1)</td>
<td>0.1182 (-2)</td>
<td>0.5489 (-4)</td>
<td>0.2401 (-1)</td>
<td>0.3842 (-1)</td>
</tr>
<tr>
<td></td>
<td>.88 (-1)</td>
<td>.12 (-2)</td>
<td>---</td>
<td>.238 (-1)</td>
<td>.383 (-1)</td>
<td>.11 (-1)</td>
</tr>
<tr>
<td>t</td>
<td>0.9701 (0)</td>
<td>0.4850 (0)</td>
<td>0.7234 (-1)</td>
<td>0.6742 (-2)</td>
<td>0.3542 (-1)</td>
<td>0.4055 (-1)</td>
</tr>
<tr>
<td></td>
<td>.9714 (0)</td>
<td>.4855 (0)</td>
<td>.718 (-1)</td>
<td>.73 (-2) b</td>
<td>.358 (-1)</td>
<td>.40 (-1)</td>
</tr>
</tbody>
</table>

a  These values are taken from Reference 6.

b  These values are taken from Reference 7.
TABLE III

Results for $Q(1s-1s)$, in units of $\pi a_0^2$, calculated in the $1s-2s-2p$ "close coupling" approximation. Rows are labeled by "s" for singlet and "t" for triplet results. Numbers in parentheses give the power of ten by which the preceding entry must be multiplied. The results of Burke, Schey, and Smith (Ref. 14) are shown below each entry for comparison. Omissions in the table are simply numbers that were not calculated.

<table>
<thead>
<tr>
<th>L</th>
<th>E</th>
<th>0.81</th>
<th>1.00</th>
<th>1.21</th>
<th>1.44</th>
<th>2.25</th>
<th>4.00</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s</td>
<td>0.4490 (0)</td>
<td>0.2646 (0)</td>
<td>0.1730 (0)</td>
<td>0.1277 (0)</td>
<td>0.8040 (-1)</td>
<td>0.5893 (-1)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.36869(+1)</td>
<td>0.29067(+1)</td>
<td>0.22979(+1)</td>
<td>0.18273(+1)</td>
<td>0.9947 (0)</td>
<td>0.3966 (0)</td>
</tr>
<tr>
<td>0</td>
<td>s</td>
<td>0.9600 (-2)</td>
<td>0.1001 (-1)</td>
<td>0.1325 (-1)</td>
<td>0.1042 (-1)</td>
<td>0.2052 (-2)</td>
<td>0.9244 (-2)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.17268(+1)</td>
<td>0.13711(+1)</td>
<td>0.10857(+1)</td>
<td>0.8849 (0)</td>
<td>0.5146 (0)</td>
<td>0.2427 (0)</td>
</tr>
<tr>
<td>1</td>
<td>s</td>
<td>0.4539 (-1)</td>
<td>0.6530 (-1)</td>
<td>0.3510 (-1)</td>
<td>0.4894 (-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.8579 (-1)</td>
<td>0.9327 (-1)</td>
<td>0.9386 (-1)</td>
<td>0.8455 (-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>s</td>
<td>(see text)</td>
<td>0.8150 (-2)</td>
<td>0.1002 (-1)</td>
<td>0.3946 (-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.1865 (-1)</td>
<td>0.1684 (-1)</td>
<td>0.1533 (-1)</td>
<td>0.1435 (-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>s</td>
<td>0.187 (-1)</td>
<td>0.168 (-1)</td>
<td>0.153 (-1)</td>
<td>0.143 (-1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV

Results for Q(1s-2s), in units of $\pi a_0^2$, calculated in the 1s-2s-2p "close coupling" approximation. Rows are labeled by "s" for singlet and "t" for triplet results. Numbers in parentheses give the power of ten by which the preceding entry must be multiplied. The results of Burke, Schey, and Smith (Ref. 14) are shown below each entry for comparison. Omissions in the table are simply numbers that were not calculated.

<table>
<thead>
<tr>
<th>L</th>
<th>E</th>
<th>0.81</th>
<th>1.00</th>
<th>1.21</th>
<th>1.44</th>
<th>2.25</th>
<th>4.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>0.5282 (-1)</td>
<td>0.7670 (-1)</td>
<td>0.5888 (-1)</td>
<td>0.3805 (-1)</td>
<td>0.7132 (-3)</td>
<td>0.4915 (-2)</td>
</tr>
<tr>
<td></td>
<td>.529 (-1)</td>
<td>.766 (-1)</td>
<td>.588 (-1)</td>
<td>.380 (-1)</td>
<td>.123 (-1)</td>
<td>.49 (-2)</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>0.1280 (-1)</td>
<td>0.3715 (-2)</td>
<td>0.5128 (-2)</td>
<td>0.5491 (-2)</td>
<td>0.2127 (-1)</td>
<td>0.3053 (-2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.12 (-1)</td>
<td>.36 (-2)</td>
<td>.51 (-2)</td>
<td>.55 (-2)</td>
<td>.45 (-2)</td>
<td>.30 (-2)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>s</td>
<td>0.4409 (-2)</td>
<td>0.1447 (-1)</td>
<td>0.2460 (-1)</td>
<td>0.2558 (-1)</td>
<td>0.3091 (-1)</td>
<td>0.1520 (-1)</td>
</tr>
<tr>
<td></td>
<td>.45 (-2)</td>
<td>.145 (-1)</td>
<td>.246 (-1)</td>
<td>.256 (-1)</td>
<td>.309 (-1)</td>
<td>.153 (-1)</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>0.6928 (-1)</td>
<td>0.1225 (0)</td>
<td>0.1002 (0)</td>
<td>0.7170 (-1)</td>
<td>0.3360 (-1)</td>
<td>0.1542 (-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.709 (-1)</td>
<td>.1219 (0)</td>
<td>.1000 (0)</td>
<td>.716 (-1)</td>
<td>.335 (-1)</td>
<td>.154 (-1)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>s</td>
<td>0.5950 (-1)</td>
<td>0.8208 (-1)</td>
<td>0.2451 (-1)</td>
<td>0.9420 (-1)</td>
<td>0.245 (-1)</td>
<td>0.942 (-1)</td>
</tr>
<tr>
<td></td>
<td>.581 (-1)</td>
<td>.823 (-1)</td>
<td>.245 (-1)</td>
<td>.942 (-1)</td>
<td>0.3016 (-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>0.2856 (-2)</td>
<td>0.2090 (-1)</td>
<td>0.3583 (-1)</td>
<td>0.358 (-1)</td>
<td>0.302 (-1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.31 (-2)</td>
<td>.211 (-1)</td>
<td>.358 (-1)</td>
<td>.302 (-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>s</td>
<td>(see text)</td>
<td>0.1028 (-1)</td>
<td>0.2472 (-1)</td>
<td>0.4040 (-2)</td>
<td>0.247 (-1)</td>
<td>0.40 (-2)</td>
</tr>
<tr>
<td></td>
<td>.103 (-1)</td>
<td></td>
<td>.247 (-1)</td>
<td>.40 (-2)</td>
<td>0.36 (-2)</td>
<td>.70 (-2)</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>0.1738 (-1)</td>
<td>0.2075 (-1)</td>
<td>0.3590 (-2)</td>
<td>0.6997 (-2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.175 (-1)</td>
<td>.208 (-1)</td>
<td>.36 (-2)</td>
<td>.70 (-2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE V

Results for Q(1s-2p), in units of $\pi a_0^2$, calculated in the 1s-2s-2p "close coupling" approximation. Rows are labeled by "s" for singlet and "t" for triplet results. Numbers in parentheses give the power of ten by which the preceding entry must be multiplied. The results of Burke, Schey, and Smith (Ref. 14) are shown below each entry for comparison. Omissions in the table are simply numbers that were not not calculated.

<table>
<thead>
<tr>
<th>L</th>
<th>E</th>
<th>0.81</th>
<th>1.00</th>
<th>1.21</th>
<th>1.44</th>
<th>2.25</th>
<th>4.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>0.3858 (-1)</td>
<td>0.3593 (-1)</td>
<td>0.3588 (-1)</td>
<td>0.3427 (-1)</td>
<td>0.7522 (-2)</td>
<td>0.3537 (-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.384 (-1)</td>
<td>0.360 (-1)</td>
<td>0.359 (-1)</td>
<td>0.343 (-1)</td>
<td>0.171 (-1)</td>
<td>0.35 (-2)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.6820 (-3)</td>
<td>0.3319 (-2)</td>
<td>0.6819 (-2)</td>
<td>0.9555 (-2)</td>
<td>0.2146 (-1)</td>
<td>0.5226 (-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7 (-3)</td>
<td>0.33 (-2)</td>
<td>0.68 (-2)</td>
<td>0.95 (-2)</td>
<td>0.106 (-1)</td>
<td>0.52 (-2)</td>
</tr>
<tr>
<td>1</td>
<td>s</td>
<td>0.7445 (-1)</td>
<td>0.1106 (0)</td>
<td>0.1104 (0)</td>
<td>0.8137 (-1)</td>
<td>0.1754 (-1)</td>
<td>0.2346 (-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.754 (-1)</td>
<td>0.1105 (0)</td>
<td>0.1105 (0)</td>
<td>0.815 (-1)</td>
<td>0.176 (-1)</td>
<td>0.24 (-2)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.6735 (-1)</td>
<td>0.7945 (-1)</td>
<td>0.6277 (-1)</td>
<td>0.4164 (-1)</td>
<td>0.1325 (-1)</td>
<td>0.3804 (-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.657</td>
<td>0.798 (-1)</td>
<td>0.629 (-1)</td>
<td>0.416 (-1)</td>
<td>0.133 (-1)</td>
<td>0.38 (-2)</td>
</tr>
<tr>
<td>2</td>
<td>s</td>
<td>0.1086 (0)</td>
<td>0.2527 (0)</td>
<td>0.2894 (0)</td>
<td>0.9420 (-1)</td>
<td>0.942 (-1)</td>
<td>0.942 (-1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1095 (0)</td>
<td>0.2332 (0)</td>
<td>0.2895 (0)</td>
<td>0.942 (-1)</td>
<td>0.942 (-1)</td>
<td>0.942 (-1)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.7614 (-2)</td>
<td>0.4605 (-1)</td>
<td>0.5372 (-1)</td>
<td>0.3572 (-1)</td>
<td>0.357 (-1)</td>
<td>0.357 (-1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.83 (-2)</td>
<td>0.458 (-1)</td>
<td>0.537 (-1)</td>
<td>0.357 (-1)</td>
<td>0.357 (-1)</td>
<td>0.357 (-1)</td>
</tr>
<tr>
<td>3</td>
<td>s</td>
<td>(see text)</td>
<td>0.3517 (-1)</td>
<td>0.1256 (0)</td>
<td>0.9987 (-1)</td>
<td>0.999 (-1)</td>
<td>0.999 (-1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.353 (-1)</td>
<td>0.1256 (0)</td>
<td>0.999 (-1)</td>
<td>0.999 (-1)</td>
<td>0.999 (-1)</td>
<td>0.999 (-1)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.5023 (-1)</td>
<td>0.1672 (0)</td>
<td>0.1741 (0)</td>
<td>0.1077 (0)</td>
<td>0.1077 (0)</td>
<td>0.1077 (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.505</td>
<td>0.1671 (0)</td>
<td>0.1740 (0)</td>
<td>0.1077 (0)</td>
<td>0.1077 (0)</td>
<td>0.1077 (0)</td>
</tr>
</tbody>
</table>
TABLE VI

Results for Q(2s-2s), in units of $\pi a_o^2$, calculated in the 1s-2s-2p "close coupling" approximation. Rows are labeled by "s" for singlet and "t" for triplet results. Numbers in parentheses give the power of ten by which the preceding entry must be multiplied. The results of Burke, Schey, and Smith (Ref. 14) are shown below each entry for comparison. Omissions in the table are simply numbers that were not calculated.

<table>
<thead>
<tr>
<th>L</th>
<th>E</th>
<th>0.81</th>
<th>1.00</th>
<th>1.21</th>
<th>1.44</th>
<th>2.25</th>
<th>4.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>0.78309(+1)</td>
<td>0.2883 (0)</td>
<td>0.6587 (-1)</td>
<td>0.1670 (0)</td>
<td>0.4708 (0)</td>
<td>0.2415 (0)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.78133(+1)</td>
<td>0.2876 (0)</td>
<td>0.654 (-1)</td>
<td>0.1665 (0)</td>
<td>0.3737 (0)</td>
<td>0.2412 (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.16222(+1)</td>
<td>0.63092(+1)</td>
<td>0.23016(+1)</td>
<td>0.17179(+1)</td>
<td>0.12223(+1)</td>
<td>0.7893 (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.16236(+1)</td>
<td>0.62512(+1)</td>
<td>0.23015(+1)</td>
<td>0.17193(+1)</td>
<td>0.13909(+1)</td>
<td>0.7894 (0)</td>
</tr>
<tr>
<td>1</td>
<td>s</td>
<td>0.14636(+2)</td>
<td>0.6917 (0)</td>
<td>0.10485(+1)</td>
<td>0.10842(+1)</td>
<td>0.10736(+1)</td>
<td>0.4973 (0)</td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.14697(+2)</td>
<td>0.6943 (0)</td>
<td>0.10493(+1)</td>
<td>0.10828(+1)</td>
<td>0.10734(+1)</td>
<td>0.4968 (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11614(+1)</td>
<td>0.17218(+2)</td>
<td>0.12868(+2)</td>
<td>0.91693(+1)</td>
<td>0.41908(+1)</td>
<td>0.16552(+1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11596(+1)</td>
<td>0.17219(+2)</td>
<td>0.12867(+2)</td>
<td>0.91722(+1)</td>
<td>0.41917(+1)</td>
<td>0.16547(+1)</td>
</tr>
<tr>
<td>2</td>
<td>s</td>
<td>0.22294 (0)</td>
<td>0.31521(+1)</td>
<td>0.21047(+1)</td>
<td>0.11931(+1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.22204 (0)</td>
<td>0.31518(+1)</td>
<td>0.21036(+1)</td>
<td>0.11929(+1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.90319(+2)</td>
<td>0.30624(+2)</td>
<td>0.89754(+1)</td>
<td>0.38700(+1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.90320(+2)</td>
<td>0.30629(+2)</td>
<td>0.89735(+1)</td>
<td>0.38692(+1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>s</td>
<td>(see text)</td>
<td>0.43127(+1)</td>
<td>0.9910 (0)</td>
<td>0.7178 (0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>t</td>
<td>0.19736(+2)</td>
<td>0.12949(+2)</td>
<td>0.53647(+1)</td>
<td>0.26707(+1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.20372(+2)</td>
<td>0.12943(+2)</td>
<td>0.53636(+1)</td>
<td>0.26697(+1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER THREE
CHAPTER THREE. METHOD FOR TREATING
LONG RANGE INTERACTIONS IN THE NONITERATIVE
INTEGRAL EQUATION FORMALISM

This Chapter is composed of a manuscript which has been submitted recently to the Journal of Chemical Physics as a companion article to the preceding one. It shows that equations furnished by the noniterative integral equation method can be used to construct a procedure for including the effects of long range potential "tails" into a calculation in which the potential has been truncated at \( r_N \). In particular, sets of integrals which determine the \( R \) matrix may be treated as vectors, and a certain matrix \( \Omega \) applied to these vectors has the effect of "projecting" their values at \( r_N \) over the potential tail to give corrected values. The \( \Omega \) matrix, actually an infinite series, carries the iterative structure of the scattering equations and hence formally resembles a Born series development of the integrals involved. A two term approximation, \( \Omega_1 \), is considered, and explicit expressions derived for a potential of the form

\[
V_{ij} = \sum_\lambda C_{ij\lambda} r^{-\lambda-1}.
\]

This approximation is applied to the long range \( r^{-2} \) and \( r^{-3} \) potential terms in the close coupled calculations of electron-hydrogen atom scattering and found to give very good results.
1. THEORY

Consider a scattering system whose description has been reduced to a coupled set of $N_{\nu}$ one dimensional differential equations for the radial scattering functions

$$B(\nu|r)F(\nu\nu^o|r) = \sum_{\nu'} U(\nu\nu'|r) F(\nu'|\nu^o|r),$$  \hspace{1cm} (1)

where $B(\nu|r)$ is the free wave differential operator for channel $\nu$,

$$B(\nu|r) = \frac{d^2}{dr^2} - \frac{\ell_{\nu}(\ell_{\nu} + 1)}{r^2} + k_{\nu}^2.$$  \hspace{1cm} (2)

Scattering from channel $\nu^o$ to channel $\nu$ is described by the function $F(\nu\nu^o|r)$. All channels are assumed to be open. It will also be assumed that the physical potential which gave rise to the matrix $U(\nu\nu'|r)$ decreases more rapidly than $1/r$. Because of this assumption, there is some asymptotic region in which the $F(\nu\nu^o|r)$ look like phase-shifted spherical waves for a free particle

$$F(\nu\nu^o|r) \sim k_{\nu}^{-\frac{3}{2}}$$

$$\times [\delta(\nu\nu^o) \sin(k_{\nu}r - \ell_{\nu}\pi/2) + \mathcal{R}(\nu\nu^o) \cos(k_{\nu}r - \ell_{\nu}\pi/2)]$$  \hspace{1cm} (3)

From a numerical point of view, this means it is possible to choose a number $r_{\infty}$ such that Eq. (3) can be written as an equality to within a specified degree of accuracy for all $r > r_{\infty}$. The value of $r_{\infty}$ may be called the "effective infinity" for the problem. This procedure is equivalent to decomposing the potential function as

$$U(\nu\nu'|r) = U_0(\nu\nu'|r) + U_1(\nu\nu'|r),$$  \hspace{1cm} (4)
where

\[ U_0(\nu'\nu' | r) \equiv U(\nu'\nu' | r), \quad r \leq r_\infty \]  \hspace{1cm} (5a)

\[ U_1(\nu'\nu' | r) \equiv U(\nu'\nu' | r), \quad r > r_\infty \]  \hspace{1cm} (5b)

and then setting all the \( U_1 \) to zero.

There is a second infinity in the problem. It will be called the "practical infinity", \( r_N \), and it depends in large part on a number of factors external to the actual problem. When one employs a numerical procedure to calculate the radial scattering functions, the continuous coordinate \( r \) is replaced by a discrete set of points \( \{ r_i \} \). Since the resources (principally computer time) available for solving the problem are finite, there can only be a finite number of \( r_i \) used. Let this number be \( N \). In addition, the precision desired in the results dictates the maximum spacings between \( r_i \) and \( r_{i+1} \). The largest value of \( r_N \), then, constitutes the "practical infinity" for the calculation.

For many problems, \( r_\infty < r_N \). There are, unfortunately, a number of very interesting problems for which \( r_\infty > r_N \). This suggests a further decomposition of the potential,

\[ U_0(\nu'\nu' | r) = V(\nu'\nu' | r) + \hat{V}(\nu'\nu' | r), \]  \hspace{1cm} (6)

where

\[ V(\nu'\nu' | r) \equiv U(\nu'\nu' | r), \quad r \leq r_N ; \]  \hspace{1cm} (7a)

\[ \hat{V}(\nu'\nu' | r) \equiv U(\nu'\nu' | r), \quad r_N < r \leq r_\infty ; \]  \hspace{1cm} (7b)

By hypothesis, therefore, the solution of

\[ \mathcal{S}(\nu | r) \mathcal{F}(\nu'\nu' | r) = \sum_{\nu'} U_0(\nu'\nu' | r) \mathcal{F}(\nu'\nu' | r) \]  \hspace{1cm} (8)
cannot be practically constructed, but the truncated problem with $U_0$ replaced by $V$ can be solved. It is the purpose of this article to establish a relationship between these two problems within the context of the noniterative integral equation technique.\(^1\)

A formal expression for $F$ may be given in terms of the Green function for $\mathcal{S}(\nu|r)$,\(^2\)

$$G(\nu|\mathbf{r}, \mathbf{r'}) = F(\nu|\mathbf{r}) G(\nu|\mathbf{r'}), \tag{9}$$

where $\mathbf{r}$ ($\mathbf{r'}$) is the lesser (greater) of $\mathbf{r}$ and $\mathbf{r'}$.

The component functions of $G$ are defined by

$$F(\nu|\mathbf{r}) = k_{\nu}^{\frac{1}{2}} r j(k_{\nu} r) \tag{10a}$$

$$G(\nu|\mathbf{r}) = -k_{\nu}^{\frac{1}{2}} r n(k_{\nu} r) \tag{10b}$$

where $j(k_{\nu} r)$ and $n(k_{\nu} r)$ are the spherical Bessel and Neumann functions, respectively. The radial scattering solutions are

$$F(\nu_\theta|\mathbf{r}) = \delta(\nu_\theta r) F(\nu|\mathbf{r}) + \int_0^\infty G(\nu|\mathbf{r}, \mathbf{r'}) \sum_{\nu'} U_0(\nu_\theta|\mathbf{r'}) F(\nu'|\mathbf{r'}) d\mathbf{r'} \tag{11}$$

Eliminating the dependence of $G$ on $\mathbf{r}$ and $\mathbf{r'}$ gives

$$F(\nu_\theta|\mathbf{r}) = F(\nu|\mathbf{r}) C(\nu_\theta) + G(\nu|\mathbf{r}) A(\nu_\theta|\mathbf{r}) - F(\nu|\mathbf{r}) B(\nu_\theta|\mathbf{r}), \tag{12}$$

where

$$A(\nu_\theta|\mathbf{r}) = \int_0^\infty F(\nu|\mathbf{r'}) \sum_{\nu'} U_0(\nu_\theta|\mathbf{r'}) F(\nu'|\mathbf{r'}) d\mathbf{r'}, \tag{13a}$$

$$B(\nu_\theta|\mathbf{r}) = \int_0^\infty G(\nu|\mathbf{r'}) \sum_{\nu'} U_0(\nu_\theta|\mathbf{r'}) F(\nu'|\mathbf{r'}) d\mathbf{r'}, \tag{13b}$$
and

\[ C(\nu \nu^0) = \delta(\nu \nu^0) + B(\nu \nu^0) \]  \hspace{1cm} (13c)

The definition of \( C(\nu \nu^0) \) employs the convention of omitting the argument of a function (\( B \) in this case) when it is to be evaluated at \( r = \infty \). Here, it is more convenient to use a simple matrix notation. A straightforward rule, which is easily verified for these equations, is to replace all doubly subscripted functions and constants by square matrices, and singly subscripted quantities by diagonal matrices. Equations (12) and (13) then read

\[ \underline{F}(r) = \underline{F}(r) \cdot \underline{C} + \underline{G}(r) \cdot \underline{A}(r) - \underline{F}(r) \cdot \underline{B}(r) \]  \hspace{1cm} (14)

where

\[ \underline{A}(r) = \int_{0}^{r} \underline{F}(r') \cdot \underline{U}_0 (r') \cdot \underline{F}(r') dr' , \]  \hspace{1cm} (15a)

\[ \underline{B}(r) = \int_{0}^{r} \underline{G}(r') \cdot \underline{U}_0 (r') \cdot \underline{F}(r') dr' , \]  \hspace{1cm} (15b)

\[ \underline{C} = \underline{I} + \underline{B} \]  \hspace{1cm} (15c)

where \( \underline{I} \) is the \( N \times N \) identity matrix. Now, by making the substitution

\[ \underline{F}(r) = \underline{F}^0(r) \cdot \underline{C} \]  \hspace{1cm} (16)

in Eq. (14), it is found (for non-singular \( \underline{C} \)) that \( \underline{F}^0 \) satisfies the equation.

\[ \underline{F}^0(r) = \underline{F}(r) + \underline{G}(r) \cdot \underline{A}^0(r) - \underline{F}(r) \cdot \underline{B}^0(r) \]  \hspace{1cm} (17)
where

\[ A^\circ(r) = \int_0^r F(r') \cdot U_0(r') \cdot \tilde{F}^\circ(r') dr', \]  

\[ B^\circ(r) = \int_0^r G(r') \cdot U_0(r') \cdot \tilde{F}^\circ(r') dr'. \]  

As previously discussed, the solution to Eq. (17) can be simply stepped out from the origin, subject to the initial condition

\[ \tilde{F}^\circ(0) = 0. \]  

In order to derive useful scattering information, the asymptotic form of \( \tilde{F}(r) \) is needed. This is easily found from Eq. (11) to be

\[ \tilde{F}(r) = \tilde{F}(r) + G(r) \cdot A, \quad r > r_\infty \]  

The properties of \( j(\ell|\rho) \) and \( n(\ell|\rho) \) can be used to show that

\[ F(\nu|r) \xrightarrow{r \to \infty} k_\nu^{-\frac{1}{2}} \sin(k_\nu r - \ell \sqrt{\nu} \pi/2), \]  

\[ G(\nu|r) \xrightarrow{r \to \infty} -k_\nu^{-\frac{1}{2}} \cos(k_\nu r - \ell \sqrt{\nu} \pi/2). \]  

From a comparison of Eqs. (3) and (20), it is evident that the \( R \) matrix is

\[ \tilde{R} = -A = -A^\circ \cdot C \]  

Using \( \tilde{B} = B^\circ \cdot C \) to solve Eq. (15c) for \( \zeta \), this can be written in terms of calculated integrals as

\[ \tilde{R} = A^\circ \cdot [B^\circ - 1]^{-1} \]
Consider again the calculation which is feasible. If \( \mathbf{V} \) is set equal to \( Q \), this is equivalent to stopping the integration of Eq. (17) at \( r = r_N \). The \( R \) matrix for the potential \( \mathbf{V} \) will then be given by

\[
R(r_N) = A^o(r_N) \cdot [B^o(r_N) - 1]^{-1}.
\]

(24)

In the remainder of this section, a method will be developed for obtaining (approximately) the values of \( A^o \) and \( B^o \) from their values at \( r_N \).

Applying the rule for differentiating an integral, it is seen that the functions \( \dot{A}^o(r) \) and \( \dot{B}^o(r) \) satisfy the differential equations

\[
\frac{d}{dr} \dot{A}^o(r) = \frac{F(r) \cdot U_o(r) \cdot F^o(r)}{\dot{A}^o(r)}, \quad (25a)
\]

\[
\frac{d}{dr} [\dot{B}^o(r) - 1] = \frac{G(r) \cdot U_o(r) \cdot F^o(r)}{\dot{B}^o(r) - 1}. \quad (25b)
\]

Using Eq. (17), it is possible to write a single matrix differential equation

\[
\frac{d}{dr} \dot{P}(r) = M(r) \cdot \dot{P}(r) \quad (26)
\]

where

\[
\dot{P}(r) = \begin{bmatrix} \dot{A}^o(r) \\ \dot{B}^o(r) - 1 \end{bmatrix}
\]

(27)

and

\[
M(r) = \begin{bmatrix} F(r) \cdot U_o(r) \cdot G(r) & - F(r) \cdot U_o(r) \cdot F(r) \\ G(r) \cdot U_o(r) \cdot G(r) & - G(r) \cdot U_o(r) \cdot F(r) \end{bmatrix}
\]

(28)
Equation (26) may be integrated between the limits \( r_1 \) and \( r_2 \), and the result expressed as \(^3\)

\[
\mathcal{P}(r_2) = \Omega(r_2, r_1) \cdot \mathcal{P}(r_1).
\]  

(29)

The matrix \( \Omega \) is called the "matricant", and is given by the series

\[
\Omega(r_2, r_1) = 1 + \int_{r_1}^{r_2} \frac{M(r)dr}{r} + \int_{r_1}^{r_2} \frac{[M(r) \cdot \int_{r_1}^{r} M(r')dr']dr}{r} + \ldots
\]

(30)

In this equation, \( \mathcal{I} \) is the \( 2N \times 2N \) identity. A property of \( \Omega \) is that for every closed interval in which \( M(r) \) is continuous, the series in Eq. (30) is absolutely and uniformly convergent.

All that is necessary now is to choose \( r_1 = r_N \) and \( r_2 = r_\infty \). Then the sought-after connection is stated

\[
\begin{bmatrix}
\check{A}^0(r_\infty) \\
\check{B}^0(r_\infty) - 1
\end{bmatrix} = \Omega(r_\infty, r_N) \cdot \begin{bmatrix}
\check{A}^0(r_N) \\
\check{B}^0(r_N) - 1
\end{bmatrix}.
\]  

(31)

It should be pointed out that this result is just a Born series expansion of the \( \check{A} \) and \( \check{B} \) integrals for \( \check{V} \), starting with the solution for \( \check{V} \). The beauty of Eq. (31) is that the structure of the iterative solution of Eq. (25) is clearly separated from the initial values \( \mathcal{P}(r_N) \). A convenient interpretation of this equation is that the application of the matrix \( \Omega \) "projects" the values of the integrals at \( r_N \) to their values at \( r_\infty \). For this reason, the method will be referred to as the "projection method."
If \( \tilde{\Omega} \) is written in terms of partitioned \( N \times N \) submatrices,

\[
\tilde{\Omega} = \begin{bmatrix}
\Omega_{11} & \Omega_{12} \\
\Omega_{21} & \Omega_{22}
\end{bmatrix},
\]

an explicit relationship between \( \mathcal{R} \) and \( \mathcal{R}_N \equiv \mathcal{R}(r_N) \) may be written,\(^4\) namely

\[
\mathcal{R} = [\Omega_{11} \cdot \mathcal{R}_N + \Omega_{12}] \cdot [\Omega_{21} \cdot \mathcal{R}_N + \Omega_{22}]^{-1}.
\]

(33)

There are three important characteristics of this method to be noted. First, it must be approximate in practice. Although Eq. (31) is exact, the true matricant \( \tilde{\Omega} \) cannot be calculated any more easily than the solution for the full potential can. However, it will be shown in the third section of this paper that the first approximation,

\[
\Omega_1(r_\infty, r_N) \equiv 1 + \int_{r_N}^{r_\infty} M(r)dr,
\]

(34)
can give very good results; yet it is simple enough to be easily computed.

Second, the procedure deals directly with the integrals which determine \( \mathcal{R} \), rather than with the wavefunction itself. This seems to be a natural state of affairs for the integral equation method, though it certainly would not be difficult to use the asymptotic matching technique which has been developed from the differential equation method.\(^5,6\) To do this, one would evaluate the matrix

\[
\tilde{\mathcal{F}}(r_N) = \tilde{\mathcal{F}}(r_N) - \mathcal{G}(r_N) \cdot \mathcal{R}(r_N)
\]

and then match to an asymptotic form for \( \tilde{\mathcal{F}} \) which is appropriate to the potential \( \tilde{\mathcal{V}} \). The matching requires the calculation and inversion of an \( N \times N \) matrix, which is essentially equivalent to the construction of \( \tilde{\Omega}(r_\infty, r_N) \).
Third, an especially attractive feature of the projection method is that it can be applied immediately to any reasonable potential, so long as the integral of $\mathcal{M}$ can be evaluated. This may very well be the principle advantage of the method, that it may be readily applied to cases for which the asymptotic form of $\mathcal{F}$ is extremely complicated or may not even have a known analytic form.
2. APPLICATION TO ELECTRON-HYDROGEN ATOM SYSTEM

In this section, the application of Eq. (31) to the calculation of cross sections in the close coupled exchange approximation for the electron-hydrogen atom system will be described. The details of performing that calculation with the integral equation method are given in the preceding paper; a short outline here is sufficient for the present discussion. Let \( \nu = [n \ell_1 \ell_2] \) be the index of the various open channels. The bound electron has quantum numbers \( n \) and \( \ell_1 \), and the free electron has partial wave angular momentum \( \ell_2 \). The full wave function is expanded in terms of H atom basis states and radial scattering functions in a representation which has been coupled to give eigenfunctions of the total angular and spin momenta, \( \mathbf{L}^2 \) and \( \mathbf{S}^2 \). The equations describing the radial functions for the free electron may be written schematically as

\[
\mathcal{F}(\nu|\mathbf{r}) \mathcal{F}(\nu'\rho|\mathbf{r}) = \sum_{\nu'} U_0(\nu\nu'|\mathbf{r}) \mathcal{F}(\nu'\rho|\mathbf{r}) + U_{\text{exp}}(\nu\rho|\mathbf{r})
\]  

(36)

where \( U_{\text{exp}} \) represents both direct and exchange potential terms which decay exponentially with increasing \( \mathbf{r} \). The potential \( U_0 \) is

\[
U_0(\nu\nu'|\mathbf{r}) = \sum_{\lambda} C_\lambda(\nu\nu') \mathbf{r}^{-\lambda-1}.
\]

(37)

In this equation, the \( C'_s \) are constants, symmetric with respect to the indices \( \nu \) and \( \nu' \), and the sum is over all \( \lambda \) consistent with the triangle inequalities \( \Delta (\lambda \ell_1 \ell_1') \) and \( \Delta (\lambda \ell_2 \ell_2') \). All of the \( \lambda = 0 \) terms are identically zero. The dipole and higher order multipoles arise when non-spherical atomic basis states are used in the expansion of the full wave function. Note that when only s states are present, all of the \( U_0 \) are zero; for the exponentially decaying potential, the inequality \( r_\infty < r_N \) is easily satisfied.
The integro-differential equations (36) are transformed into sets of Volterra equations for auxiliary functions \( F_1(r) \),

\[
F_1(r) = \frac{\partial F_0}{\partial r} + \nabla(r) \cdot A_1(r) - F(r) \cdot B_1(r),
\]

(38)

which can be integrated outward numerically from the origin. The functions \( A_1 \) and \( B_1 \) are

\[
A_1(r) = \int_0^r F(r') \cdot \psi_1(r') dr',
\]

(39a)

\[
B_1(r) = \int_0^r G(r') \cdot \psi_1(r') dr',
\]

(39b)

where

\[
\psi_1(r) = U_\infty(r) \cdot \frac{F(r)}{F(r)} + \{\text{terms from } U_{\text{exp}}\}
\]

(40)

A cutoff value \( r_c \) can be specified such that all the terms in \( U_{\text{exp}} \) have diminished to an entirely negligible magnitude. Then for \( r > r_c \), the equations go over in the form shown in Eqs. (17) and (18).

Since \( r_c \) can easily be less than \( r_N \), the projection method may be used to complete the calculation. The only modification necessary is in the definition of \( P_\delta \), which must be extended to include all the \( A \) and \( B \) type integrals. In the notation of the preceding paper,

\[
P(r) = \begin{bmatrix} A^\circ(r) & \hat{A}(r) \\ \hat{A}(r) & B^\circ(r) \end{bmatrix}
\]

(41)

Two features of this problem make it a useful example. In the first place, long range components of interaction potentials can often be expressed in the form of Eq. (37). For this reason, the formulae developed in the Appendix should be readily useful for a number of problems. In the second place, and perhaps more importantly, there are "exact"
results for this calculation which are available for comparison. The
calculations of Burke, Schey, and Smith,\textsuperscript{7} using a 1s, 2s, 2p basis on
hydrogen, made use of a special asymptotic form which represents exactly
the form of $\mathcal{R}$ appropriate to the potential $U_0'$, and to which their cal-
culated wavefunctions could be matched. The coefficients in the
matching could be calculated to any desired accuracy with their recursion
formulae. Their results, therefore, will be used as a standard by which
the present method may be judged.

There are two types of observations which may be made that provide
internal checks on the procedure as well. These are the symmetry of the
calculated $\mathcal{R}$ matrix, and the convergence of $\mathcal{R}$ with respect to increasing
$r_N$. An inspection of the second order term in Eq. (3) shows that for the
potential $U_0'$, the largest terms which have been neglected by using
$\Omega_\perp$ in place of $\Omega$ are of order $O(r_N^{-2})$. Thus, for larger $r_N$, $\Omega_\perp$ should
become a better approximation to $\Omega$. Also, within the first order approxi-
mation, increasing $r_N$ has the effect of decreasing the amount of potential
for which correction is being made. For these two reasons, it is expected
that using larger values of $r_N$ will cause the transformed integrals to
approach more nearly their exact $r_\infty$ values, and $\mathcal{R}$ should be observed
to converge to a constant matrix.

Lack of symmetry in $\mathcal{R}$ is characterized by an "asymmetry parameter,"

$$
\alpha = \text{Max} \left| \left[ \mathcal{R}(vv') - \mathcal{R}(v'v) \right]/\mathcal{R}(vv') \right|.
$$

(42)

When double precision arithmetic is used for the computations, $\mathcal{R}(r_N)$
is always symmetric to nine decimal places. Thus, $\alpha$ will indicate how
much symmetry is lost during the projection procedure, and it is expected
to decrease with increasing $r_N$. 
3. RESULTS FOR ELECTRON-HYDROGEN ATOM SYSTEM

The details of the calculations have been given in the preceding paper. Tables I and II show values of the upper triangular elements of $R_N$ and $R$ at several $r_N$ for calculations on two different states of the electron-hydrogen atom scattering system. The convention for labelling the channels is that of Burke, Schey, and Smith.\(^7\) For each matrix element, the first row entries are the values at $r_N$, while the second row entries are the results of the projection method. The last line in each table contains the values of $\alpha$ for the $R$ matrices at each $r_N$. In the column headed "BSS" are the matrix elements of Burke, Schey, and Smith.\(^7\)

Both effects, the convergence of $R$ and the decrease in $\alpha$, are readily apparent. It is remarkable, however, that even at $r_N = 40$ the projection procedure does so well. A most striking example is the $(2,2)$ element in Table I.

One notes that as $r_N$ increases, the elements of $R$ do not converge in a strictly monotonic fashion, but rather they seem to show a small amount of oscillation, usually between $r_N = 40$ and $r_N = 120$. This is understandable since both the $A$ and $B$ integrals and $\Omega_1$ have a damped oscillatory nature. Such behavior in the results could probably be nearly eliminated by including the second order term in $\Omega$, since for the exact $\Omega$ the projected integrals would truly be constants.

In general, the cross sections themselves are not as sensitive to the values of the integrals as the $R$ matrix elements are, though the same trends are still readily apparent. In Tables III and IV are the cross sections corresponding to the $R$ matrices in Tables I and II. A general property of all of the three and four channel calculations with the present method on this problem is that three of the four cross sections
computed at \( r_N = 40 \) will be reasonably close to the BSS values, while the fourth one may be in error by 20% or more. After the projection procedure is used, all four are usually quite close to the BSS results.

4. CONCLUSIONS

The projection procedure developed in Section I of this paper to take into account the effects of long range potentials is a technique which is easily applied in its first approximation form and seems capable of yielding accurate numerical results. Since the computation time required to apply the projection method is quite small (on the order of magnitude of the time required to include 40 additional quadrature points) it is anticipated that this procedure will significantly extend the range of problems to which the noniterative integral equation technique may be conveniently applied.
APPENDIX

In order to construct $\Omega$, it is necessary to evaluate the integrals

$$
\mathcal{T}(R) = \int_{R}^{\infty} M(r) dr = \begin{bmatrix}
T_{11}(R) & -T_{12}(R) \\
T_{21}(R) & -T_{22}(R)
\end{bmatrix}, \quad (A1)
$$

where

$$
T_{11}(\nu' \nu | R) = \int_{R}^{\infty} G(\nu | r) U_{o}(\nu \nu' | r) (\nu' | r) dr, \quad (A2)
$$

$$
T_{12}(\nu' \nu | R) = \int_{R}^{\infty} F(\nu | r) U_{o}(\nu \nu' | r) (\nu' | r) dr, \quad (A3)
$$

$$
T_{21}(\nu' \nu | R) = \int_{R}^{\infty} G(\nu | r) U_{o}(\nu \nu' | r) (\nu' | r) dr, \quad (A4)
$$

and $T_{22}(\nu' \nu | R) = T_{11}(\nu' \nu | R)$. In addition, note that $T_{12}(\nu' \nu | R) = T_{12}(\nu' \nu | R)$ and $T_{21}(\nu' \nu | R) = T_{21}(\nu' \nu | R)$. Thus, only half of the integrals in $\mathcal{T}$ actually need to be calculated. The limits in Eq. (A1) should be noted. The upper limit, $r_{\infty}$, was defined to be large enough that the primitives in Eqs. (A2)-(A4) are essentially zero there. This is certainly true if $r_{\infty}$ is replaced by $\infty$. The lower limit, $R$, is any point where the numerical integration is stopped.

In deriving expressions for the $T_{ij}$, use is made of the following formulae for the Riccati-Bessel functions:
\[ F(\nu|r) = \sum_{m=0}^{\ell_2} [R(\nu|m) \sin k_\nu r + S(\nu|m) \cos k_\nu r] r^{-m}, \quad (A5) \]
\[ G(\nu|r) = \sum_{m=0}^{\ell_2} [S(\nu|m) \sin k_\nu r - R(\nu|m) \cos k_\nu r] r^{-m}, \quad (A6) \]

where the coefficients are found from
\[ R(\nu|m) + i S(\nu|m) = i^{m-\ell_2}(\ell_2+m)![(\ell_2-m)!2^m m!]^{-1} k_\nu^{-m-\frac{3}{2}} \quad (A7) \]

By using Eqs. (A5), (A6), and (37) in (A2), there results the formula
\[ T_{11}(\nu\nu'|R) = \sum_{m_1} \sum_{m_2} \sum_{\lambda} C_\lambda (\nu\nu') \]
\[ \times [R(\nu|m_2)S(\nu'|m_1)E_M(\nu\nu'|R) - R(\nu|m_2)R(\nu'|m_1)F_M(\nu\nu'|R) \]
\[ + S(\nu|m_2)S(\nu'|m_1)F_M(\nu\nu'|R) - S(\nu|m_2)R(\nu'|m_1)G_M(\nu\nu'|R)], \quad (A8) \]

with similar expressions for \( T_{12} \) and \( T_{21} \), where the summation indices are \( 0 \leq m_1 \leq \ell_1 \) and \( 0 \leq m_2 \leq \ell_2 \). The subscript is \( M \equiv m_1 + m_2 + \lambda \).

The \( E, F, \) and \( G \) functions are defined by
\[ E_M(\nu\nu'|R) = \int_{R}^{\infty} r^{-M-1} \sin k_\nu r \sin k_{\nu'} r \, dr, \quad (A9) \]
\[ F_M(\nu\nu'|R) = \int_{R}^{\infty} r^{-M-1} \sin k_\nu r \cos k_{\nu'} r \, dr, \quad (A10) \]
\[ G_M(\nu\nu'|R) = \int_{R}^{\infty} r^{-M-1} \cos k_\nu r \cos k_{\nu'} r \, dr. \quad (A11) \]

Considering the definitions of \( R(\nu|m) \) and \( S(\nu|m) \), it can be seen that for any \( m_1, m_2, \lambda \) combination in the summation for \( T_{4j} \), there can be only one non-zero product in the braces.

The required integrals may be easily evaluated in terms of the auxiliary functions
\[ C_M(K|R) = \int_{R}^{\infty} r^{-M-1} \cos Kr \, dr, \quad (A12) \]
\[ S_M(K|R) = \int_R^\infty r^{-M-1} \sin K r \, dr. \]  
(A13)

Integration by parts of these expressions gives a recursive method for generating the strings, \( C_M(K|R) \) and \( S_M(K|R) \), for \( 1 \leq M \leq \ell_2 + \ell_2' + \ell_{\max} \):

\[ C_M(K|R) = -R^{-M}(KR)^{-1} \sin KR + (M+1)^{-1}S_{M+1}(K|R), \]  
(A14)

\[ S_M(K|R) = R^{-M}(KR)^{-1} \cos KR - (M+1)^{-1}C_{M+1}(K|R). \]  
(A15)

For the special case of \( K = 0 \),

\[ C_M(0|R) = (M R^{M})^{-1}, S_M(0|R) = 0. \]  
(A16)

In terms of these functions, the \( E, F, \) and \( G \) integrals may then be calculated from

\[ E_M(\nu \nu' | R) = \frac{1}{2} \left[ C_M(k_v - k_{\nu'}, | R) - C_M(k_{\nu'} + k_{\nu'}, | R) \right], \]  
(A17)

\[ F_M(\nu \nu' | R) = \frac{1}{2} \left[ S_M(k_v - k_{\nu'}, | R) + S_M(k_{\nu'} + k_{\nu'}, | R) \right], \]  
(A18)

\[ G_M(\nu \nu' | R) = \frac{1}{2} \left[ C_M(k_v - k_{\nu'}, | R) + C_M(k_{\nu'} + k_{\nu'}, | R) \right]. \]  
(A19)
REFERENCES

   W. N. Sams and D. J. Kouri, J. Chem. Phys., 51, 4815 (1969);


4. An equation analogous to Eq. (31) can be derived which relates $R$
   and $R_N$ directly. It is impractical, however, since it requires
   an integration over the inverse of the matricant constructed for
   $F \cdot u_0 \cdot G$.


TABLE I

\( R \)-matrix elements for \( L=0 \) singlet, \( E = 1.21 \) Rydberg. For each element, the first line is \( R_N(vv') \) computed with the values at \( r_N \) of the integrals. The second line is \( R(vv') \) computed with the projected values of the integrals. At the bottom of each column, the asymmetry parameter \( \alpha \) (see Eq. (42) in text) for that \( R \) matrix is given. The column labeled "BSS" contains the results of Reference 7. Numbers in parentheses give the power of ten by which the preceding entry should be multiplied.

<table>
<thead>
<tr>
<th>( r^*_N )</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1,1) )</td>
<td>.1607(0)</td>
<td>.1539(0)</td>
<td>.1514(0)</td>
<td>.1494(0)</td>
<td>.1497(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1498(0)</td>
<td>.1486(0)</td>
<td>.1489(0)</td>
<td>.1488(0)</td>
<td>.1488(0)</td>
<td>.1443(0)</td>
</tr>
<tr>
<td>( (1,2) )</td>
<td>.6673(0)</td>
<td>.5923(0)</td>
<td>.5636(0)</td>
<td>.5494(0)</td>
<td>.5408(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5024(0)</td>
<td>.5043(0)</td>
<td>.5049(0)</td>
<td>.5050(0)</td>
<td>.5051(0)</td>
<td>.5051(0)</td>
</tr>
<tr>
<td>( (1,4) )</td>
<td>.1508(+1)</td>
<td>.1575(+1)</td>
<td>.1594(+1)</td>
<td>.1604(+1)</td>
<td>.1607(+1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1610(+1)</td>
<td>.1620(+1)</td>
<td>.1620(+1)</td>
<td>.1621(+1)</td>
<td>.1621(+1)</td>
<td>.1632(+1)</td>
</tr>
<tr>
<td>( (2,2) )</td>
<td>-.1757(-1)</td>
<td>-.8048(-1)</td>
<td>.1097(0)</td>
<td>.1228(0)</td>
<td>.1299(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1558(0)</td>
<td>.1559(0)</td>
<td>.1559(0)</td>
<td>.1559(0)</td>
<td>.1559(0)</td>
<td>.1545(0)</td>
</tr>
<tr>
<td>( (2,4) )</td>
<td>-.1112(+1)</td>
<td>-.8440(0)</td>
<td>-.7384(0)</td>
<td>-.6844(0)</td>
<td>-.6529(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-.5216(0)</td>
<td>-.5202(0)</td>
<td>-.5208(0)</td>
<td>-.5206(0)</td>
<td>-.5208(0)</td>
<td>-.5242(0)</td>
</tr>
<tr>
<td>( (4,4) )</td>
<td>-.5484(+1)</td>
<td>-.5741(+1)</td>
<td>-.5800(+1)</td>
<td>-.5824(+1)</td>
<td>-.5834(+1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-.5862(+1)</td>
<td>-.5870(+1)</td>
<td>-.5869(+1)</td>
<td>-.5870(+1)</td>
<td>-.5870(+1)</td>
<td>-.5914(+1)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>.0117</td>
<td>.0030</td>
<td>.0013</td>
<td>.0008</td>
<td>.0005</td>
<td></td>
</tr>
</tbody>
</table>
TABLE II

$R$-matrix elements for $L = 2$ singlet, $E = 2.25$ Rydberg. For each element, the first line is $R_N^{(\nu\nu')}$ computed with the values at $r_N$ of the integrals. The second line is $R^{(\nu\nu')}$ computed with the projected values of the integrals. At the bottom of each column, the asymmetry parameter $\alpha$ (see Eq. (42) in text) for that $R$ matrix is given. The column labeled "BSS" contains the results of Reference 7.

<table>
<thead>
<tr>
<th>$r_N$</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^{(\nu\nu')}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,1)</td>
<td>.4799(-1)</td>
<td>.4769(-1)</td>
<td>.4766(-1)</td>
<td>.4771(-1)</td>
<td>.4773(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.4770(-1)</td>
<td>.4772(-1)</td>
<td>.4772(-1)</td>
<td>.4772(-1)</td>
<td>.4772(-1)</td>
<td>.474(-1)</td>
</tr>
<tr>
<td>(1,2)</td>
<td>-.5790(-1)</td>
<td>-.5322(-1)</td>
<td>-.5155(-1)</td>
<td>-.5075(-1)</td>
<td>-.5027(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-.4818(-1)</td>
<td>-.4824(-1)</td>
<td>-.4826(-1)</td>
<td>-.4826(-1)</td>
<td>-.4826(-1)</td>
<td>-.482(-1)</td>
</tr>
<tr>
<td>(1,3)</td>
<td>-.3443(0)</td>
<td>-.3452(0)</td>
<td>-.3453(0)</td>
<td>-.3455(0)</td>
<td>-.3457(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-.3458(0)</td>
<td>-.3460(0)</td>
<td>-.3461(0)</td>
<td>-.3461(0)</td>
<td>-.3461(0)</td>
<td>-.3461(0)</td>
</tr>
<tr>
<td>(1,4)</td>
<td>.7342(-1)</td>
<td>.7193(-1)</td>
<td>.7176(-1)</td>
<td>.7163(-1)</td>
<td>.7147(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.7125(-1)</td>
<td>.7106(-1)</td>
<td>.7101(-1)</td>
<td>.7100(-1)</td>
<td>.7100(-1)</td>
<td>.710(-1)</td>
</tr>
<tr>
<td>(2,2)</td>
<td>.7838(0)</td>
<td>.7761(0)</td>
<td>.7732(0)</td>
<td>.7717(0)</td>
<td>.7708(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.7671(0)</td>
<td>.7670(0)</td>
<td>.7670(0)</td>
<td>.7670(0)</td>
<td>.7670(0)</td>
<td>.7669(0)</td>
</tr>
<tr>
<td>(2,3)</td>
<td>.1296(0)</td>
<td>.1304(0)</td>
<td>.1299(0)</td>
<td>.1298(0)</td>
<td>.1297(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1289(0)</td>
<td>.1291(0)</td>
<td>.1291(0)</td>
<td>.1290(0)</td>
<td>.1290(0)</td>
<td>.1290(0)</td>
</tr>
<tr>
<td>(2,4)</td>
<td>.5183(-1)</td>
<td>.7344(-1)</td>
<td>.8060(-1)</td>
<td>.8435(-1)</td>
<td>.8649(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.9515(-1)</td>
<td>.9543(-1)</td>
<td>.9537(-1)</td>
<td>.9539(-1)</td>
<td>.9538(-1)</td>
<td>.955(-1)</td>
</tr>
<tr>
<td>(3,3)</td>
<td>.1203(+1)</td>
<td>.1210(+1)</td>
<td>.1212(+1)</td>
<td>.1212(+1)</td>
<td>.1213(+1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1215(+1)</td>
<td>.1215(+1)</td>
<td>.1215(+1)</td>
<td>.1215(+1)</td>
<td>.1215(+1)</td>
<td>.1215(+1)</td>
</tr>
<tr>
<td>(3,4)</td>
<td>-.2965(0)</td>
<td>-.2939(0)</td>
<td>-.2927(0)</td>
<td>-.2920(0)</td>
<td>-.2916(0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-.2907(0)</td>
<td>-.2900(0)</td>
<td>-.2899(0)</td>
<td>-.2898(0)</td>
<td>-.2898(0)</td>
<td>-.2899(0)</td>
</tr>
<tr>
<td>(4,4)</td>
<td>.5937(-1)</td>
<td>.6138(-1)</td>
<td>.6239(-1)</td>
<td>.6301(-1)</td>
<td>.6339(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.6511(-1)</td>
<td>.6507(-1)</td>
<td>.6506(-1)</td>
<td>.6506(-1)</td>
<td>.6506(-1)</td>
<td>.648(-1)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>.0065</td>
<td>.0017</td>
<td>.0008</td>
<td>.0004</td>
<td>.0003</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III

Cross sections corresponding to $R$ matrix in Table I. Organization here parallels Table I.

<table>
<thead>
<tr>
<th>$r_N$</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q(n\ell \rightarrow n'\ell')$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1s-1s</td>
<td>.1726(0)</td>
<td>.1730(0)</td>
<td>.1731(0)</td>
<td>.1730(0)</td>
<td>.1730(0)</td>
<td>.1722(0)</td>
</tr>
<tr>
<td></td>
<td>.1731(0)</td>
<td>.1730(0)</td>
<td>.1730(0)</td>
<td>.1730(0)</td>
<td>.1730(0)</td>
<td></td>
</tr>
<tr>
<td>1s-2s</td>
<td>.5818(-1)</td>
<td>.5853(-1)</td>
<td>.5862(-1)</td>
<td>.5872(-1)</td>
<td>.5875(-1)</td>
<td>.588(-1)</td>
</tr>
<tr>
<td></td>
<td>.5821(-1)</td>
<td>.5873(-1)</td>
<td>.5882(-1)</td>
<td>.5886(-1)</td>
<td>.5888(-1)</td>
<td></td>
</tr>
<tr>
<td>1s-2p</td>
<td>.3703(-1)</td>
<td>.3624(-1)</td>
<td>.3612(-1)</td>
<td>.3612(-1)</td>
<td>.3604(-1)</td>
<td>.359(-1)</td>
</tr>
<tr>
<td></td>
<td>.3547(-1)</td>
<td>.3580(-1)</td>
<td>.3584(-1)</td>
<td>.3586(-1)</td>
<td>.3588(-1)</td>
<td></td>
</tr>
<tr>
<td>2s-2s</td>
<td>.8854(-1)</td>
<td>.7596(-1)</td>
<td>.7231(-1)</td>
<td>.7055(-1)</td>
<td>.6960(-1)</td>
<td>.654(-1)</td>
</tr>
<tr>
<td></td>
<td>.6597(-1)</td>
<td>.6584(-1)</td>
<td>.6586(-1)</td>
<td>.6586(-1)</td>
<td>.6587(-1)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV

Cross sections corresponding to $R$ matrix in Table II. Organization here parallels Table II.

<table>
<thead>
<tr>
<th>$n \ell \rightarrow n' \ell'$ Q</th>
<th>$r_N$</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s-1s</td>
<td>.4924(-2)</td>
<td>.4904(-2)</td>
<td>.4891(-2)</td>
<td>.4891(-2)</td>
<td>.4895(-2)</td>
<td>.49(-2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.4892(-2)</td>
<td>.4894(-2)</td>
<td>.4894(-2)</td>
<td>.4894(-2)</td>
<td>.4894(-2)</td>
<td>.49(-2)</td>
<td></td>
</tr>
<tr>
<td>1s-2s</td>
<td>.2165(-2)</td>
<td>.1794(-2)</td>
<td>.1676(-2)</td>
<td>.1620(-2)</td>
<td>.1587(-2)</td>
<td>.15(-2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1450(-2)</td>
<td>.1453(-2)</td>
<td>.1455(-2)</td>
<td>.1455(-2)</td>
<td>.1455(-2)</td>
<td>.15(-2)</td>
<td></td>
</tr>
<tr>
<td>1s-2p</td>
<td>.9388(-1)</td>
<td>.9393(-1)</td>
<td>.9394(-1)</td>
<td>.9402(-1)</td>
<td>.9408(-1)</td>
<td>.942(-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.9411(-1)</td>
<td>.9418(-1)</td>
<td>.9420(-1)</td>
<td>.9420(-1)</td>
<td>.9420(-1)</td>
<td>.942(-1)</td>
<td></td>
</tr>
<tr>
<td>2s-2s</td>
<td>.1234(+1)</td>
<td>.1216(+1)</td>
<td>.1208(+1)</td>
<td>.1205(+1)</td>
<td>.1202(+1)</td>
<td>.1193(+1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.1193(+1)</td>
<td>.1193(+1)</td>
<td>.1193(+1)</td>
<td>.1193(+1)</td>
<td>.1193(+1)</td>
<td>.1193(+1)</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER FOUR
CHAPTER FOUR. NUMERICAL STUDIES AND COMPUTATIONAL PROCEDURES

The purpose of this Chapter is to present additional material which may be combined with Chapters Two and Three to completely document the present study. This information is conveniently presented in three parts.

Section 1 describes the procedure used to integrate the scattering equations. The numerical algorithm employed was the repeated trapezoidal rule.

In Section 2, the convergence studies are discussed, and the detailed numerical results are presented. This includes final \( R \) matrices and cross sections as well as those obtained in the determination of convergence of the calculations with respect to various parameters. These results give the justification for the parameter values used in Chapter Two, and indicate the precision which may be expected in the final results.

In order to complete the record for the present application of the noniterative integral equation technique, Section 3 contains a description of the program which performed these calculations. Equations and algorithms for computing the required coefficients and functions are given, with reference to the program listing in the Appendix.
1. TRAPEZOIDAL RULE ALGORITHM

The equations derived in Chapter Two were integrated by application of the repeated trapezoidal rule. Such a low order algorithm was used for two reasons, one positive and one negative. On the positive side, the rule is very easy to program. Furthermore, it will be seen shortly that only one quadrature point at a time needs to be considered. This reduces storage requirements and simplifies the working equations.

On the negative side, there had been no evidence indicating that the algorithmic error of the trapezoidal rule had ever been responsible for false answers. One could therefore hope that any difficulty in obtaining results would not have its source in the integration scheme.

It thus seemed reasonable to use this simplest of schemes to investigate the present method. The results which were obtained here can be regarded as a posteriori justification of our choice.

The working equations which result from applying the trapezoidal rule to Eqs. (50) - (53) of Chapter Two are now derived. To demonstrate the method, it is sufficient to consider a single representative equation of each type. With an obvious simplification of notation,

\[ F(R) = \phi(R) + G(R)A(R) - F(R)B(R), \]  \hspace{1cm} (1.1)

where

\[ A(R) = \int_{0}^{R} F(r)W(r)dr, \]  \hspace{1cm} (1.2)

\[ B(R) = \int_{0}^{R} G(r)W(r)dr, \]  \hspace{1cm} (1.3)
and the function in the integrands is given schematically by

\[ W(r) = V(r)F(r) + 2g_\lambda P(r) r^\lambda X(r). \]  \hfill (1.4)

Also, for the exchange function,

\[ X(R) = U(R) - R^{-2\lambda - 1} Q(R) \]  \hfill (1.5)

with

\[ U(R) = \int_0^R r^{-\lambda - 1} P(r)F(r)dr, \]  \hfill (1.6)

\[ Q(R) = \int_0^R r^\lambda P(r)F(r)dr. \]  \hfill (1.7)

The continuous variable \( R \) is now replaced by a set of equi-spaced quadrature points. If \( \Delta \) denotes the step size, then

\[ R \to \{ R_n \}, \quad R_n = n\Delta. \]

When a function \( F(R) \) is evaluated at the \( i \)-th quadrature point, it will be denoted by

\[ F_i \equiv F(R_i). \]

Consider first Eq. (1.1). According to the previous remarks, it may be written

\[ F_{i+1} = \phi_{i+1} + G_{i+1} A_{i+1} - F_{i+1} B_{i+1}. \]  \hfill (1.8)

The trapezoidal rule gives the values of \( A_{i+1} \) and \( B_{i+1} \) by

\[ A_{i+1} = \frac{1}{2} \Delta F_0 W_0 + \sum_{j=1}^{i} \Delta F_j W_j + \frac{1}{2} \Delta F_{i+1} W_{i+1} \]  \hfill (1.9a)
\begin{equation}
B_{i+1} = \frac{1}{2} \Delta G_{0,0} W_0 + \sum_{j=1}^i \Delta G_{j,j} W_j + \frac{1}{2} \Delta G_{i+1,i+1} W_{i+1}.
\end{equation}

(1.9b)

Because the last terms in \( A_{i+1} \) and \( B_{i+1} \) cancel when the expressions are substituted into Eq. (1.8), these "integrals" may be replaced by the quantities

\begin{equation}
A_{i}^* = A_{0}^* + \sum_{j=1}^i \Delta F_{j,j} W_j, \quad A_{0}^* = \frac{1}{2} \Delta F_{0,0} W_0,
\end{equation}

(1.10a)

\begin{equation}
B_{i}^* = B_{0}^* + \sum_{j=1}^i \Delta G_{j,j} W_j, \quad B_{0}^* = \frac{1}{2} \Delta G_{0,0} W_0.
\end{equation}

(1.10b)

The radial function \( F_{i+1} \) may then be calculated from \( A_{i}^* \) and \( B_{i}^* \), rather than \( A_{i+1} \) and \( B_{i+1} \).

Obtaining \( W_{i+1} \) from \( F_{i+1} \) requires the integration of Eq. (1.5).

In terms of quadrature points

\begin{equation}
X_{i+1} = U_{i+1} - R_{i+1}^{-2\lambda-1} Q_{i+1}
\end{equation}

(1.11)

and application of the trapezoidal rule gives

\begin{equation}
U_{i+1} = \frac{1}{2} \Delta R^{-\lambda-1} P_{0,0} F_0 + \sum_{j=1}^i \Delta R_{j}^{-\lambda-1} P_{j,j} F_j + \frac{1}{2} \Delta R_{i+1}^{-\lambda-1} P_{i+1} F_{i+1},
\end{equation}

(1.12)

and similarly for \( Q_{i+1} \), with \( R^{-\lambda-1} \) replaced by \( R^{\lambda} \). It is again convenient to define the related quantities

\begin{equation}
U_{i}^* = U_{0}^* + \sum_{j=1}^i \Delta R_{j}^{-\lambda-1} P_{j,j} F_j, \quad U_{0}^* = \frac{1}{2} \Delta R_{0}^{-\lambda-1} P_{0,0} F_0,
\end{equation}

(1.13a)

\begin{equation}
Q_{i}^* = Q_{0}^* + \sum_{j=1}^i \Delta R_{j}^{-\lambda} P_{j,j} F_j, \quad Q_{0}^* = \frac{1}{2} \Delta R_{0}^{\lambda} P_{0,0} F_0.
\end{equation}

(1.13b)
One can then write the two numerically equivalent expressions

\[ X_{i+1} = U_{i+1} - R_{i+1}^{-2\lambda - 1} Q_{i+1} \]

\[ = U_{i+1} - R_{i+1}^{-2\lambda - 1} Q_{i+1} \]  \hspace{1cm} (1.14)

Having established the preceding relations, a statement of the complete algorithm can now be made. Given the values of the "integrals" \( A_{i}, B_{i}, U_{i}, \) and \( Q_{i} \), the following steps will integrate the scattering equations from \( R_{i} \) to \( R_{i+1} \).

1) The functions \( \phi_{i+1}, F_{i+1}, \) and \( G_{i+1} \) are known; calculate

\[ F_{i+1} = \phi_{i+1} + G_{i+1} A_{i} - F_{i+1} B_{i} \]  \hspace{1cm} (1.15)

2) The function \( P_{i+1} \) is known; calculate

\[ U_{i+1} = U_{i} + \Delta R_{i+1}^{-\lambda - 1} P_{i+1} F_{i+1} \]  \hspace{1cm} (1.16)

\[ Q_{i+1} = Q_{i} + \Delta R_{i+1}^\lambda P_{i+1} F_{i+1} \]  \hspace{1cm} (1.17)

3) The function \( V_{i+1} \) is known; calculate

\[ W_{i+1} = V_{i+1} F_{i+1} + 2g_{\lambda} P_{i+1} (R_{i+1}^\lambda U_{i+1} - R_{i+1}^{-\lambda - 1} Q_{i+1}) \]  \hspace{1cm} (1.18)

4) Calculate

\[ A_{i+1} = A_{i} + \Delta F_{i+1} W_{i+1} \]  \hspace{1cm} (1.19)

\[ B_{i+1} = B_{i} + \Delta G_{i+1} W_{i+1} \]  \hspace{1cm} (1.20)
At each step, the indicated operations are carried out for all functions of that type. It can be seen that with this algorithm, only the current values of \( A_1^*, B_1^*, U_1^*, \) and \( Q_1^* \) need be stored at any time.

A consideration of the algorithm presented shows that at the conclusion of each cycle, the \( A^*, B^*, U^*, \) and \( Q^* \) values are a "half-step ahead" of the values the \( A, B, U, \) and \( Q \) integrals would have; i.e., in each case, the last value of the integrand has been added to the previous integral value with a factor of \( \Delta \) rather than \( \frac{1}{2} \Delta \). This fact is of importance when the step size changes across a quadrature point. If the step size between \( R_i \) and \( R_{i+1} \) is \( \Delta_\alpha \), and the step size between \( R_{i+1} \) and \( R_{i+2} \) is \( \Delta_\beta \), then the integration from \( R_i \) to \( R_{i+1} \) is modified by using the factor \( \frac{1}{2}(\Delta_\alpha + \Delta_\beta) \) for this step. For example,

\[
A_1^* = A_{i-1}^* + \Delta_\alpha F_i W_i ,
\]

\[
A_{i+1}^* = A_i^* + \frac{1}{2}(\Delta_\alpha + \Delta_\beta) F_{i+1} W_{i+1} ,
\]

\[
A_{i+2}^* = A_{i+1}^* + \Delta_\beta F_{i+2} W_{i+2} .
\]

It can be seen that this artifice permits the same algorithm to be used for a variable step size scheme as well as for a fixed step size scheme. In particular, this technique is what was used to connect the inner and outer regions of integration for the present calculations.

To start the integration, a statement of the initial conditions is required. In Chapter Two, these conditions were given as

\[
F_0 = 0, \text{ for all } F_\xi(R) .
\]
However, one needs in addition to specify the values of $A_0^*$, $B_0^*$, $U_0^*$, and $Q_0^*$. Due to the singularity in $V(R)$, the values to be assigned to these integrands at the origin may or may not be zero.

This question occasioned a small study of the equations in the especially simple case of single channel s-wave scattering from the hydrogen $1s$ state. For this problem, there is one "direct" function $F^0(R)$ and one "exchange" function $F^1(R)$. The relevant equations are exactly Eqs. (1.1) - (1.7) of this chapter, with $\lambda = 0$, $g_o = (-1)^{1-s}$, and supplemented by the definitions

$$V(r) = -2(1 + \frac{1}{r}) e^{-2r}, \quad (\text{1.23})$$

$$P(r) = 2r e^{-r}, \quad (\text{1.24})$$

$$F(r) = k^{-\frac{1}{2}} \sin kr, \quad (\text{1.25})$$

$$G(r) = -k^{-\frac{1}{2}} \cos kr. \quad (\text{1.26})$$

The two inhomogeneous functions in the Volterra equations are

$$\phi(r) = F(r) \quad (\text{1.27a})$$

for $F^0$, and

$$\phi(r) = cr e^{-r} + c^2 e^{-r} - c^2 \cos kr, c = \frac{2}{1 + k^2} \quad (\text{1.27b})$$

For $F^1$.

The obvious technique for examining the behavior at the origin is to expand the equations in a power series. Equations (1.23) - (1.27) admit of immediate expansions, and one needs only assume an expansion
for $F^\alpha$, $\alpha = 0$ or 1, to begin. The series adopted here is

$$F^\alpha(r) = \sum_{n=0}^{\infty} a_n(\alpha) r^{n+m},$$

(1.28)

where $m$ is an index to be determined. At this stage, $m$ is not restricted; the $F^\alpha$ may have singularities in them as long as

$$F(r) = C F^0(r) + D F^1(r)$$

(1.29)

goes to zero at the origin.

Working through steps 2, 3, and 4 of the algorithm, using Eq. (1.28) and expansions of the known functions around $r = 0$, one finds that $m$ must be greater than zero if the divergent form $\int_0^R r^{-1} \, dr$ is to be avoided. Using Eq. (1.1) with $\phi(r) = F(r)$, it is found that all terms may be accounted for if $m = 1$. Furthermore, for $F^0$,

$$a_0(0) = k^{1/2}.$$  

(1.30)

If Eq. (1.27b) for $\phi(r)$ is used in Eq. (1.1), it is again found that $m = 1$, and

$$a_0^{(1)} = c(1 - c) = 2 \frac{1 - k^2}{(1 + k^2)^2}.$$  

(1.31)

The final results of this exercise are that

$$A_o^* = 0, \quad U_o^* = 0, \quad Q_o^* = 0,$$

(1.32)

and

$$B_o^* = k^{-1/2} \Delta a_0^*(0).$$

(1.33)
It would certainly be convenient just to set $B_0^* = 0$ always, particularly for the more complicated two, three, and four channel calculations. Although it would seem to be an insignificant error in Eq. (1.10b) to ignore the $B_0^*$ contribution, the fact is that all other terms in that expression depend indirectly on $B_0^*$. For instance, to calculate $B_1^*$ requires $W_1$, which in turn requires $F_1$. From Eq. (1.15),

$$F_1 = \phi_1 - F_1 B_0^*.$$  \hspace{1cm} (1.34)

Thus, neglect of $B_0^*$ leads to erroneous values of $F_1$, which leads to erroneous values of $U_1^*$, $Q_1^*$, and $W_1$. Finally, $A_1^*$ and $B_1^*$ will be in error, and consequently so will $F_2$, etc.

In the absence of an analytical study of error propagation for this algorithm, a simple numerical test was made to determine the actual resultant error for a particular case. The phase shift for scattering in the singlet $L = 0$ state at $E = 1.0$ was calculated with $B_0^* = 0$ and found to be identical with the correct value to better than eight significant digits. This was a single precision computation on a Burroughs 5500 machine. It was concluded that for all calculations in the future, this simplification could be used freely.
2. CONVERGENCE STUDIES AND DETAILED RESULTS

It must be emphasized that the goal of this study was not to produce the most comprehensive and precise set of $R$ matrices and cross sections to date for various approximations to electron-hydrogen atom scattering, but rather to investigate the usefulness of the present method for this problem. The degree of convergence which was obtained with respect to various integration parameters will be discussed to give an indication of the precision obtained in this study. Full advantage of the program's flexibility was not taken in order to find the very best compromise between precision and computation time. Though desirable, this maximum efficiency was not of paramount importance since extensive calculations of cross sections were not going to be made. Nevertheless, a criterion of reasonable efficiency was used when comparing the results from several sets of input parameters to decide which set should be used for the bulk of the calculations.

The convergence studies which were done are described in the following paragraphs. The discussions are ordered according to increasing complexity of the calculation—-one channel, two channel, three and four channel. Selection of the parameters for each of these cases will be described on the basis of the results obtained from various computer trials. Final results calculated with the chosen parameters are also tabulated.

In what follows, a simple notation has been used to specify the integration parameters associated with a given calculation. Integration with step size $\Delta_\alpha$ from zero to $R_\alpha$ is denoted by $(\Delta_\alpha/R_\alpha)$. If the integration is continued to $R_\beta$ with step size $\Delta_\beta$, the parameters for the
second region are merely appended to those for the first region as
\[(\Delta_a / R_a) (\Delta_b / R_b)\].

As previously described, the integration can be interrupted at any quadra
ture point \(R_N\) and the current values of the integrals used to compute \(R\) matrices and cross sections. Usually this is done at several points before the end of the integration in order to observe convergence of the results with respect to range.

In the partial wave theory of electron-hydrogen atom scattering, the expan
sion states are grouped into eigenstates of \(L, S\), and parity of \(l_1 + l_2\). For a given atomic basis, this determines a set of coupled scattering channels. The conventions for labeling the channels in the various approximations are given in Table I. All calculations reported here are for states having \(l_1 + l_2 - L\) even. This fact is important only in the 1s-2s-2p case, for which the channel \((2, 1, L)\) has \(l_1 + l_2 - L\) odd and is hence uncoupled from the others. Calculations for this channel have not been included in this study.

In order to simplify labeling in the tables, cross sections have been written as matrix elements. The convention used is \(Q_{11} = Q(1s - 1s)\), \(Q_{12} = Q(1s - 2s)\), \(Q_{13} = Q(1s - 2p)\), and \(Q_{22} = Q(2s - 2s)\).

One Channel Calculations. The 1s Exchange Approximation

Phase shifts in the 1s exchange approximation for several partial waves in both spin states have been known since 1933.\(^1\) A summary of results from more recent calculations is given a review by Burke and Smith.\(^2\) Also, some very precise \(L = 0\) results are given by Sams and Kouri\(^3\) in their original paper on the method. The reason for our
repeating these calculations was to check the program and to develop a feel for the computational phase of the project. The reason for discussing these calculations, however, is to introduce a scheme which proved to be quite successful throughout the study for determining the extent of convergence with respect to step size.

From both the present calculations and those of Sams and Kouri, it is known that triplet phase shifts are more precisely calculated than are singlet phase shifts for the same choice of parameters. Thus, almost all attention here is focused on the singlet case. Furthermore, the majority of calculations are for \( L = 0 \) in order to make comparison with the Sams and Kouri work. All phase shifts to be presented are given in radians.

In Table II, the singlet \( L = 0 \) phase shift at \( E = 0.5 \), calculated with five different step sizes, is given. These values show an interesting step size dependence. It will be recalled that the error term for a numerical estimate of an integral by the repeated trapezoidal rule is \( R_N \Delta^2 f'' / 12 \), where \( R_N \) is the range of integration and \( f'' \) is the second derivative of the integrand evaluated at some point in the range. 4 One might assume that a phase shift calculated with step size \( \Delta \) could be represented by a power series

\[
\delta(\Delta) = \delta(0) + \Delta + q\Delta^2 + \cdots,
\]  

(1.35)

where \( \delta(0) \) is the exact value, the value in the limit of zero step size. If the value of \( f'' \) were independent of \( \Delta \), then the integrals in the calculation would be purely quadratic in \( \Delta \), and hence, so would \( \delta \). Using the phase shifts in Table II for \( \Delta = 0.05, 0.025 \), and 0.0125, the linear and quadratic coefficients in Eq. (1.35)
were found to be

\[ \lambda = 0.1707 \times 10^{-4}, \quad q = -0.2799, \quad (1.36) \]

which strongly confirms our expectation. Note that these are not "least squares" values. They are simply meant to represent \( \delta(\Delta) \) at the chosen points.

Using the fact that \( \lambda << q \), and neglecting higher order terms in Eq. (1.35), we now formulate a "Quadratic Rule" for phase shifts:

\[ \delta(\Delta) = \delta(0) + q\Delta^2. \quad (1.37) \]

This rule may be useful in two ways. First, it can be an efficient method of obtaining very high precision results. Second, it can be used to determine the error due to the finite step size used in a calculation. Both of these applications will now be illustrated.

Using the phase shifts in Table II for \( \Delta = 0.05 \) and 0.025 yields

\[ q = -0.2797. \quad (1.38) \]

This value of \( q \) may be used in Eq. (1.37) to calculate \( \delta(0) \) from any of the \( \delta(\Delta) \). Dependence of the final result on step size may thus be nearly eliminated. The extrapolated phase shifts in Table II were obtained this way. The values are remarkably consistent, varying within only six parts in \( 10^7 \). An exception to this is the \( \Delta = 0.1 \) case. This discrepancy is almost undoubtedly due to the neglect of higher order terms in Eq. (1.35). The slight trend in \( \delta(0) \) is due to changing \( q \) when \( \lambda \) is set to zero.

This example demonstrates a highly efficient procedure. The phase shifts \( \delta(0.05) \) and \( \delta(0.025) \) can be computed in 12 seconds. Yet the application of the Quadratic Rule gives results more precise than the value of \( \delta(0.005) \), which requires 40 seconds to compute.
If a large number of phase shifts are to be computed, the Quadratic Rule may be used on a few of them to estimate the lack of precision to be expected due to using a finite step size integration. After calculating a phase shift at two step sizes to determine \( q \), the fractional error in the finite step size result is

\[
\frac{\delta(\Delta) - \delta(0)}{\delta(0)} = q\Delta^2/\delta(0).
\] (1.39)

This error has been evaluated for each of the step sizes in Table II and is given in the last column.

To further test the Quadratic Rule, it was applied to the phase shifts in Table III. For \( E = 1.0 \) and 0.01, the calculated phase shifts were used to evaluate the \( q \) coefficient. This was then used to extrapolate \( \delta(0.01) \) to \( \delta(0) \). For \( E = 0.09 \), the phase shifts \( \delta(0.05) \) and \( \delta(0.01) \) were used to calculate \( q \) and \( \delta(0) \). To test the extrapolation, the phase shift was also predicted at \( \Delta = 0.005 \) and compared with the actual calculated value. At \( R_N = 15 \) and 20, agreement was exact, while at \( R_N = 10 \), there was a fractional error of 0.000014.

The last column of Table III shows the estimate of fractional error due to employing the step size \( \Delta = 0.01 \). In all cases it is less than one part in \( 10^4 \). If the convergence with respect to \( R_N \) is examined, it is also found that \( \delta(0.01) \) always changes by less than one part in \( 10^4 \). Thus, we conclude that the parameters (0.01/15) will produce phase shifts correct to about one part in \( 10^4 \).

Various other phase shifts are presented in Table IV. The singlet phase shifts were calculated with (0.01/15). A more economical integration was used for the triplet calculations, (0.01/15)(0.05/15). These calculations require one second per 75 steps.
Two Channel Calculations. The 1s-2s Exchange Approximation

This "strong coupling" approximation represents the simplest kind of multichannel calculation on this system. To study convergence of the integration of these coupled equations with respect to step size and range, the following schemes were used:

i. \((0.05/30)\)

ii. \((0.025/30)\),

iii. \((0.0125/30)\),

iv. \((0.05/10)(0.10/30)\),

v. \((0.025/10)(0.05/30)\).

A comparison of the results from i.-iii. will give an indication of convergence with respect to step size. Integration schemes iv. and v. may then be compared with i. and ii. to see if an outer region, 10-30, can be computed with a larger step size than the inner region with no loss of precision. Exchange terms were carried throughout the integration range. The choice of 30 for the range was based on some earlier runs, and is discussed further on.

This investigation was applied to four different scattering states: singlet \(L = 1\) at \(E = 0.81\), triplet \(L = 2\) at \(E = 1.00\), singlet \(L = 1\) at \(E = 1.44\), and singlet \(L = 1\) at \(E = 2.25\). The \(R\) matrices and cross sections obtained are displayed in Table V. For each matrix element, the results at \(R_N = 20\), 25, and 30 are shown.

It proved possible to analyze step size convergence in a manner similar to that described in the single channel discussion. Denoting any of the \(R_{ij}\) or \(Q_{ij}\) by \(M\), we expect that the value \(M(A)\) calculated
with step size \( \Delta \) should be related to the exact value (i.e., that for zero step size) by

\[
M(\Delta) = M(0) + q\Delta^2.
\]  

(1.40)

Also, for any three step sizes, \( \Delta_\alpha, \Delta_\beta, \) and \( \Delta_\gamma, \)

\[
\frac{M(\Delta_\alpha) - M(\Delta_\beta)}{M(\Delta_\beta) - M(\Delta_\gamma)} = \frac{\Delta_\alpha^2 - \Delta_\beta^2}{\Delta_\beta^2 - \Delta_\gamma^2} = c
\]

Using \( \Delta_\alpha = 0.05, \Delta_\beta = 0.025, \) and \( \Delta_\gamma = 0.0125 \) gives \( c = 4 \) exactly. In Table VI, the differences \( M(\Delta_\alpha) - M(\Delta_\beta) \) and \( M(\Delta_\beta) - M(\Delta_\gamma) \) are tabulated, and one sees that, to an excellent degree, they do have a ratio of four to one. Thus, we are in the realm of validity of the Quadratic Rule, Eq. (1.40). The value of the matrix element \( M(\Delta_\beta) \) can then be extrapolated to zero step size by

\[
M(0) = M(\Delta_\beta) - \frac{1}{3} [M(\Delta_\alpha) - M(\Delta_\beta)]
\]

(1.42)

for the step sizes employed here. The results of this extrapolation for the matrix elements in each of the four states investigated are shown in the third column of Table VI. The corresponding Quadratic Rule coefficient is also shown. The last column gives the fractional error of the matrix elements computed with \( \Delta_\beta \). It is seen to be generally less than five parts in \( 10^4 \).

Returning to Table V, we now turn our attention to the results in columns iv. and v. The matrix elements here differ by very little from those in columns i. and ii., respectively. A quantitative statement may be made by calculating the fractional discrepancy between the results
of schemes ii. and v. It is found to be less than $3 \times 10^{-5}$ for all cases. Because it represented a 30% savings in computer time, scheme v. was used for the remainder of the two channel calculations.

The entries in Table V show little change as $R_N$ is increased from 25 to 30. To study in detail the convergence of the results with respect to range, Tables VII and VIII have been prepared. Table VII shows results for various $L = 0$ states. Integration scheme v. did not exhibit the desired range convergence, so these calculations were made with a scheme (0.025/10)(0.05/40), which is denoted by $v'$. $R$ matrices and cross sections were computed at $R_N = 20, 25, 30, 35,$ and 40 (except for $E = 1.44$). With this extended range of integration, it became evident that the results at $R_N = 30$ are more nearly converged than one would suspect on the basis of the results at $R_N = 20$ and 25. Fractional changes in matrix elements going from $R_N = 30$ to $R_N = 35$ are generally less than 0.005, and from $R_N = 35$ to $R_N = 40$, less than 0.001.

Convergence is much better for calculations having $L > 0$. These results are in Table VIII. It is seen that fractional changes, $f$, in matrix elements are always less than 0.0004 as $R_N$ is increased from 25 to 30, and that $f$ generally decreases as $E$ increases.

No simple extrapolation procedure could be used to estimate converged results here due to the fact that the integrals undergo rather complicated, exponentially decreasing oscillation as $R_N$ is increased. Because of this fact, one may doubt that the tabulated values actually show much at all about convergence. It might be argued that sampling results at evenly spaced intervals sort of "rides on a phase" of the
integrands, so that the integrals themselves are still oscillating while showing us nearly constant values. However, since oscillation wavelengths would be energy dependent, and we observe the same general behavior of the results at all energies, we believe that the fractional changes which were tabulated actually do give a good indication of the extent of convergence with respect to range.

The results in Table II of Chapter Two were all calculated by integration scheme v. We conclude from the studies just discussed that precision in the \( L = 0 \) results is better than 1\%, while precision in the \( L > 0 \) results is better than 0.1\%. The computer time required for these calculations was 5.6 seconds per 100 steps.

**Three and Four Channel Calculations.** The \( 1s-2s-2p \) Exchange Approximation.

Although the calculations in this approximation are much more extensive than those described in the preceding paragraphs, it has again proved possible to analyze the convergence of the results with respect to step size by the Quadratic Rule. However, the question of convergence with respect to range of integration is no longer appropriate, due to the very long range multipole terms in the potential. Rather, one must discuss convergence with respect to the "projection method" which was employed to account for the full extent of the potential without actual numerical integration.

As indicated in Table I, the \( L = 0 \) state is a special state in the \( 1s-2s-2p \) approximation, giving only three scattering channels. Although the kinds of results obtained in both the three channel and four channel
calculations are similar, the two cases will be discussed separately. The convergence studies will be described in detail for the three channel calculations, followed by a more condensed discussion of the four channel calculations.

**Three Channel \((L = 0)\) Results.**

To investigate the step size dependence of these results, sample calculations were done with the following integration schemes:

i. \((0.05/40)\),

ii. \((0.025/40)\),

iii. \((0.0125/40)\).

The \(R\) matrix elements and cross sections computed by each of these schemes for the singlet \(L = 0\) state at \(E = 0.81\) are presented in Table IX. For \(\Delta_\alpha = 0.05\), \(\Delta_\beta = 0.025\), and \(\Delta_\gamma = 0.0125\), we again expect the \(c = 4\) ratio,

\[
\left[ \frac{M(\Delta_\alpha) - M(\Delta_\beta)}{M(\Delta_\beta) - M(\Delta_\gamma)} \right] = 4,
\]

(1.43)

to be satisfied if the Quadratic Rule is to be applicable. In Table X, the matrix element differences are seen to satisfy the ratio test quite well. The matrix elements \(M(\Delta_\beta)\) have thus been extrapolated to zero step size and the fractional error due to the finite step size \(\Delta_\beta\) evaluated. We find a slightly larger error than before, on the order of six parts in \(10^4\). Unless noted otherwise, all calculations hereafter will be done with \(\Delta = 0.025\) in the inner region.

The data was available for performing the step size analysis for a range of 30. However, when this was tried, it was found that the differences in calculated matrix elements failed miserably to satisfy the
c = 4 ratio. Yet the results at 40 did satisfy it. The cause of this
anomalous behavior is not known. The phenomenon may perhaps be related
to the "halfstep ahead" character of the integration when it is inter-
rupted at an interior point in the range. Since the integrands are not
yet small, this may cause erroneous matrix elements to be calculated
from the A*, B*, U*, and Q* values. However, this suggestion does not
seem compatible with the fact that perfect symmetry was still observed
in the R matrix.

The choice of the range 40 was based on the concept of convergence
with respect to part of the potential. Whereas before, all potential
terms were exponentially decreasing, the inclusion of the 2p state
gives additional terms, proportional to $R^{-2}$ and $R^{-3}$, which remain im-
portant long after the exponential terms have disappeared. The phrase,
"convergence with respect to part of the potential", means that the
results are no longer influenced by the exponential terms in the poten-
tial. Computer experiments were not performed to actually establish
that at 40 the exponentials no longer had any affect, but some simple
numerical considerations were made. Also, no attempt was made to break
the zero to 40 range into two regions of integration.

There are two places in the calculation which contain exponentially
decaying terms. One of these is a portion of the direct potential
$V_L(\nu\nu'|R)$, the other is in the terms due to exchange. The least rapidly
decaying exponential term in $V_L(\nu\nu'|R)$ is

$$
\epsilon_d(R) = \rho^{n+n'-1} e^{-\rho}, \quad \rho = \frac{n + n'}{nn'} R .
$$

(1.44)
For large $R$, this is a small number which can be calculated from

$$\varepsilon_d = \exp[(n + n' - 1)\ell_0 - \rho] .$$  \hspace{1cm} (1.45)

For $n, n' \leq 2$, we always have $\rho > R$. During integration, when $V_L$ was being calculated, each $\rho$ was checked against a cutoff value which was set to 40. If this value were exceeded, the corresponding exponential term was neglected. Evaluating $\varepsilon_d$ from Eq. (1.45) for cases of interest,

1) $n = n' = 1$, \hspace{1cm} $\varepsilon_d = 0.170 \times 10^{-15}$ ;

2) $n = 1$, $n' = 2$, \hspace{1cm} $\varepsilon_d = 0.680 \times 10^{-14}$ ;

3) $n = n' = 2$, \hspace{1cm} $\varepsilon_d = 0.272 \times 10^{-12}$ .

We note from Chapter Two that the exchange terms are of the form

$$R^\lambda \frac{P(\mu | R)}{R^\lambda} \left[ \int_0^R r^{-2\lambda-1} P(\nu | r) F_\xi(r) dr - R^{-2\lambda-1} \int_0^R r^\lambda P(\nu | r) F_\xi(r) dr \right]$$

where $\lambda$ is in the range: $\max(0, L-2) \leq \lambda \leq L + 2$. For the three channel calculations, therefore, $\lambda = 0, 1, 2$. Since both integrals in the brackets converge rather quickly to values in the range 0.05 to 50.0, the importance of exchange is given by

$$\varepsilon_x(R) = R^\lambda (R/n)^n e^{-R/n}$$ \hspace{1cm} (1.47)

for channel $\nu$ having principal quantum number $n$. Again, for large $R$, this is a small number which can be evaluated from

$$\varepsilon_x = n^\lambda \exp[(n + \lambda)\ell_0 s - s], \hspace{1cm} s = R/n.$$ \hspace{1cm} (1.48)

Various values for $R = 40$ are
1) $n = 1, \lambda = 1, \quad \epsilon_x = 0.680 \times 10^{-14}$;

   $\lambda = 2, \quad \epsilon_x = 0.272 \times 10^{-12}$;

2) $n = 2, \lambda = 1, \quad \epsilon_x = 0.330 \times 10^{-6}$;

   $\lambda = 2, \quad \epsilon_x = 0.132 \times 10^{-4}$;

   $\lambda = 3, \quad \epsilon_x = 0.528 \times 10^{-3}$.

Although $\epsilon_x$ increases with increasing $\lambda$, the integrals of $r^{-\lambda-1} P(\nu|r)F_\xi(r)$ and $r^{-\lambda} P(\nu|r)F_\xi(r)$ are found to decrease. Thus, we are not sure about the error incurred by neglecting exchange beyond 40, but it is certainly less than that in the calculations of Burke, Schey, and Smith, who neglected these terms at 30. Our error in these terms may still be on the order of $10^{-5}$ to $10^{-4}$. Table XI contains a comparison of results for the singlet $L = 0$ state at $E = 1.00$ for dropping exponential terms at 30 and at 40. The first two columns are the values of the matrix element calculated by $(0.025/30)(0.25/60)$, while the next two are the value projected from $R_N = 60$. In the first column, exponentials were neglected beyond 30, while they were carried to 40 in the second column. Although the differences are small between the two columns, the cutoff at 30 does tend to change the results in the direction of those obtained by Burke, Schey, and Smith (BSS). Most noticeable is the $R(1,2)$ value. For all calculations hereafter, the cutoff at 40 will be used.

It may be recalled that integration was carried beyond 40 in order to aid the projection method. Convergence with respect to step size in this outer region is shown in Table XII. The equations for the singlet $L = 0$ state at $E = 0.81$ were integrated according to the two
schemes

iv. \((0.025/40)(0.100/200)\),
v. \((0.025/40)(0.250/200)\).

The matrix elements at \(R_N = 200\) are given in columns one and two, while columns three and four show the results of projection from 200. One sees from the last column that the fractional error between the results of the two schemes is less than one part in \(10^4\), which is well within the precision we have maintained in the inner region.

Now that we have discussed precision in integration step sizes and cutoff parameters, we must discuss the last factor which tries to prevent our obtaining exact results, namely, the projection procedure used to account for the long range potential terms. The precision-robbing approximations in this procedure have been discussed in detail in Chapter Three, and only a few more comments will be made.

It would be more efficient computationally to be able to project accurately from small \(R_N\), say \(R_N = 40\) where the exponentials are cut off. It is our feeling that inclusion of the second integral term in \(\tilde{\Omega}\) would give an \(\tilde{\Omega}_2\) accurate enough to do this between \(40 \leq R_N \leq 60\). Unfortunately, higher order terms are very difficult to generate, although the second order is not too bad. The programming of \(\tilde{\Omega}_2\) was begun, but not completed in time to be tried for this project. This difficulty of generating more accurate approximations to \(\tilde{\Omega}\) is probably the major weakness of the method. The technique of matching to modified asymptotic forms, when it can be used, gives a simple set of recurrence relations which allow very accurate determination of the transformation matrix.
As described previously, the precision of the projection method is estimated from two parameters—the asymmetry $\alpha$ and the constancy of projected results with increasing $R_N$. Recall that $\alpha$ is the maximum fractional discrepancy from perfect symmetry of the $R$ matrix,

$$\alpha \equiv \text{Max} \left| \frac{R(\nu\nu') - R(\nu'\nu)}{R(\nu\nu')} \right|. \quad (1.49)$$

For the $R$ matrix calculated from the integrated values of the integrals, $\alpha$ is always zero. When these integrals are projected to their $R = \infty$ values, the $R$ matrix calculated from them is not perfectly symmetric, due to the approximate nature of the projection. Thus, $\alpha$ is a good measure of how inaccurate the transformation is.

Since the first order approximation, $\tilde{\Omega}_1$, errs from the exact $\Omega$ by terms of order $R_N^{-2}$, it should be possible to observe convergence in the projected results as $R_N$ is increased. Convergence is characterized by a decrease in $\alpha$ toward zero and the approach toward constant values of the matrix elements.

The results of our three channel calculations with integration scheme v. are given in Tables XIII and XIV. For a given matrix element, the first row entries in each column are the exact values of that quantity calculated by integration to the indicated $R_N$. The second row values give the results from the projection procedure applied at that $R_N$. The last line of the table gives the value of $\alpha$ for the projected $R$ matrix in each column. In the column labeled "BSS" are the values of Burke, Schey, and Smith for comparison.

The convergence in $\alpha$ values is quite evident. Furthermore, it can be seen that the projected results do tend toward constant values.
To show this tendency explicitly, Table XV has been prepared from the results in Tables XIII and XIV. Tabulated are the fractional changes in the projected matrix elements as \( R_N \) is increased. Oscillations are evident from the sign changes in a row. The four scattering states used in this table were chosen for their representative results. A quite general observation is that in nearly all cases, the least converged matrix elements are \( R(1,2) \) and \( Q(1s - 2s) \).

It was pointed out in Chapter Two that both the singlet and triplet results at \( E = 2.25 \) are in extreme disagreement with the BSS results, and seem physically in error besides. It was thought at first that the step size might be too large at this higher energy to get the desired precision. Table XVI shows the results of investigation of step size dependence of the singlet case. For each matrix element, the first row entries are the results at \( R_N = 30 \), while second row entries are results at \( R_N = 40 \). As noted in Chapter Two, the results are very confusing. Our feeling is that the problem is one of numerical error in the computer calculations. Apparently, for this \( E \) and \( L \), gross instability arises in the integration, leading to meaningless results. It was previously suggested that a stabilization procedure might be used to correct the difficulty. Calculations at both higher and lower \( E \), and at higher \( L \), showed no such difficulty.

The three channel calculations discussed in the preceding paragraphs are now summarized. Integration with scheme \( v. \) leads to step size errors on the order of six parts in \( 10^4 \). Applying the projection procedure at \( R_N = 200 \) gives \( R \) matrices whose \( \alpha \) values generally decrease with increasing energy from 0.4% at \( E = 0.81 \) to 0.01% at \( E = 4.00 \).
Also, the fractional changes in matrix elements with increasing $R_N$ are generally just a few parts in $10^4$. The overall precision to be expected is thus about $0.1 - 0.5\%$. As an example of the computation time for this scheme, consider the singlet calculation at $E = 2.25$. The time required was 19.2 seconds per 100 steps in the inner region and 4.8 seconds per 100 steps in the outer region. Each application of the projection procedure required approximately 1.65 seconds.

**Four Channel ($L > 0$) Calculations**

The most complex calculations performed were those in the $1s-2s-2p$ exchange approximation for $L = 1, 2, 3,$ and $4$. The familiar (by now) step size study was done on the singlet $L = 1$ state at $E = 1.00$. The results from integration schemes i. - iii. are contained in Table XVII, and the Quadratic Rule analysis is presented in Table XVIII.

Just as the fractional step size error for the three channel calculations was somewhat greater than that for the two channel calculations, we see here that it is larger still for a four channel calculation. From Table XVIII one finds that the fractional error for step size $\Delta \beta = 0.025$ is about one part in $10^3$. This was accepted because it seemed small enough that we could still attain our stated objectives while maintaining the same integration scheme used for the three channel work. The comparison of schemes iv. and v. was not done here. Scheme v. was used simply on the basis of its merit demonstrated earlier.

Tables XIX and XX contain the results of twelve calculations on $L = 1$ states done with scheme v. The format of presentation is the same one used for the three channel results. Concerning convergence of the projection procedure, two observations may be made.
First, \( \alpha \) values range from 0.05% to 0.9%, and there seems to be no correlation of \( \alpha \) with \( E \), at least for singlet states. Also, one usually finds that \( \alpha \) is smaller for triplet states than it is for singlet states of the same energy. The \( \alpha \) values for triplet states do appear to decrease generally as \( E \) increases. It may be noted that for some of the calculations presented here and in later tables, there is a second set of \( \alpha \) values in a footnote. This occurs four times, in two singlet and two triplet states, and at lower energies. What happened here is that all off diagonal pairs of \( R \) matrix elements were nearly equal except for the pair noted. For this one pair, one number was often a whole power of ten greater than the other. By our definition of \( \alpha \), the quantities \( [R(\nu \nu') - R(\nu' \nu)]/R(\nu \nu') \) and \( [R(\nu \nu') - R(\nu' \nu)]/R(\nu' \nu) \) could differ by a power of ten, and if \( R(\nu \nu') \) was itself small, one of these ratios could, and actually did, become a large number. Since these "spurious" values were not really indicative of the quality of the calculation, they were placed in footnotes, with the \( \alpha \) row entries being determined from the remaining elements of \( R \).

Second, one may again consider convergence of the projected values with respect to increasing the \( R_N \) from which projection was made. In Tables XIX and XX, one sees that the fractional changes in matrix elements as \( R_N \) is increased from 160 to 200 are just a few parts in \( 10^4 \).

In summary of the four channel \( L = 1 \) calculations, we feel that their precision is probably between 0.5% and 1.0% with this scheme. As an example of the computation time, consider the singlet calculation at \( E = 1.00 \). The time required was 46.7 seconds per 100 steps in the inner region and 8.8 seconds per 100 steps in the outer region. Projection required about 4.8 seconds.
As noted in Chapter Two, the calculations are their maximum size for $L > 2$. No more complete step size studies were performed. However, the singlet $L = 2$ state at $E = 0.81$ was integrated by both schemes ii. and iii. and the results placed in Table XXI. With only two calculations, the applicability of the Quadratic Rule cannot be determined, but nevertheless it was assumed to hold and was used to extrapolate the matrix elements to $\Delta = 0$. Looking at the fractional errors calculated for results from $\Delta_\alpha = 0.025$, it seems that the discrepancy has increased somewhat again over the $L = 1$ case and is about two parts in $10^3$. One may note that the Quadratic Rule coefficients are larger here. This is primarily due to the fact that the matrix elements are larger in this calculation. It is interesting that the cross sections seem to be much better than the $R$ matrix.

It will be recalled from the short discussion of the exponential cutoff at 40 that the error incurred increases for increasing $\lambda$. Because $L$ is larger for these calculations, there may well be some exchange terms whose neglect is not insignificant. Though one can raise this question for the $L = 1$ calculations as well, it is obviously more important for $L = 2, 3$, and 4. The actual problem here is that the program cut off exchange terms when $R$ exceeded 40, rather than when $R/n$ exceeded 40. Nevertheless, we have continued to use 40 for the cutoff value. Although this hinders us from giving a knowledgeable estimate of the precision in our results, we have still found good agreement between them and the BSS values. This can be seen in Tables XXII - XXVI, which contain all of our $L = 2, 3$, and 4 results.
Because of the additional channel in all of these \( L > 0 \) states, there are several more long range multipole terms for which \( \Omega \) must make correction. The matrix \( \Omega_1 \) is now \( 8 \times 8 \), and there are a total of four \( \mathbf{R}^{-2} \) terms and three \( \mathbf{R}^{-3} \) terms in \( \mathbf{V} \). In spite of these complications, the results of the projection procedure seem to be better on the whole than it was for the \( L = 0 \) and \( L = 1 \) calculations. Examination of Tables XXII - XXVI shows that \( \alpha \) again shows the general negative correlation with \( E \)--values range from 0.7% at \( E = 0.81 \) down to 0.03% at \( E = 2.25 \). Furthermore, changes in matrix elements with increasing \( R_N \) are seldom more than a few parts in \( 10^3 \), and cross sections themselves often change by only a few parts in \( 10^4 \).

In summary, consideration of step size, symmetry, and range convergences suggests that the results in Tables XXII - XXVI are within 2% of the exact values when calculated with scheme v. As an example of the computation time for this scheme, consider the singlet calculations at \( E = 1.00 \) for the various \( L \). The time required was 52.9 - 53.8 seconds per 100 steps in the outer region. Application of the projection procedure generally required 4.5 - 5.5 seconds.

There are two general conclusions of this study. The first is that quadrature errors due to finite step size may be essentially eliminated by the Quadratic Rule. When very precise results are desired, this can be an efficient method for obtaining them.

The second conclusion is that the primary source of imprecision in the three and four channel calculations is the use of the approximate matricant in the projection procedure. As pointed out before, this seems rectifiable, at least to the extent of including second order terms with little difficulty.
In connection with the projection procedure, it was noticed that often $R(\nu \nu')$ would be larger than the BSS value and $R(\nu' \nu)$ would be less. Though this was not always true, it was found to occur with a relatively high degree of consistency. Furthermore, it most often occurred when $\alpha$ values were large. This indicates the possibility that the discrepancies in the first order matricant are systematic, and it may be possible to force symmetry on the $R$ matrix using the simple prescription

$$R_{\text{sym}}(\nu \nu') = \frac{1}{2}[R(\nu \nu') + R(\nu' \nu)].$$

This has not actually been tried in this study, but is advanced here as a possible improvement. In a very recent publication, this symmetrization was used and found to definitely improve the results there.\(^6\)
3. COMPUTER ALGORITHMS AND PROGRAM

The Appendix to this Chapter contains a listing of the actual program used to obtain the results presented in Chapters Two and Three, and Section 1 of this Chapter. The purpose of this section is to act as a buffer between the reader and that listing. It will do this in two ways. First, the explicit expressions by which the necessary functions and constants were evaluated will be given. Second, the operation of the program will be broadly outlined as an aid to understanding its structure. We do not pretend excellence in this program; better programs could most certainly be written. Nevertheless, the fact remains that this one most certainly works.

Algorithms for Required Constants and Functions

To be described in this subsection are the calculation of the Green function, the atomic radial functions, the direct potential, and the angular momentum coupling coefficients. Also discussed will be the $H(\nu\mu\lambda|\mathbf{r})$ functions required in the $F_{1}$ calculations.

**Green Function**

The regular and irregular components of the Green function are easily calculated by the formulas in Messiah.\(^7\) Defining the complex sum,

$$Z(\ell|\rho) = i^{-\ell} \sum_{m=0}^{\ell} \frac{i^{m}}{2^{m}m!} \frac{(\ell + m)!}{(\ell - m)!} \rho^{-m},$$  \(2.1\)

both the Ricatti-Bessel and Neumann functions (with our normalization)
may be obtained simultaneously from

\[ F(\nu | R) = F(\ell | kR) \]
\[ = k^{-1/2} \left[ \text{Re} \, Z(\ell | kR) \sin kR + \text{Im} \, Z(\ell | kR) \cos kR \right] \quad (2.2a) \]

\[ G(\nu | R) = k^{-1/2} \left[ \text{Im} \, Z(\ell | kR) \sin kR - \text{Re} \, Z(\ell | kR) \cos kR \right] \quad (2.2b) \]

The real and imaginary parts of \( Z \) were calculated as follows. Define recursively

\[ X_{m+1} = \frac{(\ell + m + 1)(\ell - m)}{2(m + 1)\rho} \, X_m, \quad \rho = kR, \quad (2.3a) \]

\[ X_0 = 1, \quad (2.3b) \]

so that

\[ Z(\ell | \rho) = i^{-\ell} \sum_{m=0}^{\ell} i^m X_m. \quad (2.4) \]

Then one simply sums all odd terms, with alternating signs, and all even terms, again with alternating signs. Depending on \( \ell \), these two sums are assigned to the real and imaginary parts of \( Z \).

When functions for more than two successive \( \ell \) values and the same \( k \) were required, only the first two pairs were calculated by Equation (2.2). The remainder were obtained from

\[ F(\ell | kR) = \frac{2\ell - 1}{kR} \, F(\ell-1 | kR) - F(\ell-2 | kR), \quad (2.5) \]

with \( G(\nu | R) \) satisfying the same recursion relation. The quantity \( (2\ell-1)/k \) is referred to as the recursion factor.
A failing of this simple approach to the calculation of these functions is that at small \( R \) \((kR \ll \lambda)\), the cancellation that must occur in order that

\[
F(\ell | kR) \sim [k^{1/2} (2\ell + 1)!!]^{-1} (kR)^{\ell+1}
\]  

(2.6)

as \( R \to 0 \) leads to completely erroneous values. This condition only occurs for the first few quadrature points usually, and never seemed to be responsible for any noticeable error. Nevertheless, a distinct improvement in the calculating routine would be the inclusion of the appropriate asymptotic formula to avoid this problem.

**Radial Atomic Functions and the Direct Potential**

The formulas in Pauling and Wilson\(^8\) for the radial functions for hydrogenic atoms of charge \( z \) may be easily put into the form

\[
P(\nu | R) = P(n\ell | R)
\]

\[
= e^{-zR/n} \frac{R^\ell}{\ell!} \sum_{m=1}^{n-\ell} D(\nu | m) \frac{R^m}{m!},
\]  

(2.7)

where the coefficients are defined by

\[
D(\nu | m+1) = \left( -\frac{2z}{n} \right) \frac{(n-\ell-m)}{m(2\ell+m+1)} D(\nu | m),
\]  

(2.8a)

\[
D(\nu | 1) = \frac{1}{n} \frac{(2z)^\ell}{\ell!} \left[ \frac{z(n+\ell)!}{(n-\ell-1)!} \right]^{1/2} \frac{1}{2\ell + 1}.
\]  

(2.8b)

The normalization here is such that

\[
\int_0^\infty P(\nu | r) P(\nu' | r) \, dr = \delta(\nu, \nu').
\]  

(2.9)
Related to the hydrogen atom eigenvalues are the "energy coefficients"

\[ a(\nu\nu'|\lambda) = \frac{1}{2} \delta(\lambda,0)(E - E_\nu - E_{\nu'}) = \frac{1}{2} \delta(\lambda,0)(E + 1/n^2 + 1/n'^2). \quad (2.10) \]

Although the program used the general equations above for calculating the \( P(\nu|R) \), it seems that greater efficiency could be had by using a routine which had specific equations programmed for the particular radial functions desired.

The expression in Equation (2.7) can be used to derive an exact result for the integrals required in the computation of the direct potential. The general integral needed is

\[ y_\lambda(\nu\nu'|R) = R^{-\lambda-1} I_\lambda(\nu\nu'|R) - R^\lambda J_\lambda(\nu\nu'|R), \quad (2.11) \]

where

\[ I_\lambda(\nu\nu'|R) = \int_0^R r^\lambda P(\nu|r) P(\nu'|r) \, dr, \quad (2.12) \]

\[ J_\lambda(\nu\nu'|R) = \int_0^R r^{-\lambda-1} P(\nu|r) P(\nu'|r) \, dr. \quad (2.13) \]

Consider first the integral \( I_\lambda \). Using Equation (2.7) twice gives the result

\[ I_\lambda(\nu\nu'|R) = \sum_{m=1}^{n-l} \sum_{m'=1}^{n'-2} D(\nu|m) D(\nu'|m') \int_0^R e^{-\alpha r} \lambda + \lambda' + m + m' \, dr \quad (2.14) \]

where

\[ \alpha = 1/n + 1/n'. \quad (2.15) \]
Now, the indices $m$ and $m'$ only occur in the integral as their sum, $M = m + m'$. Thus, the summations over $m$ and $m'$ may be transformed into summations over $m$ and $M$. Since

$$1 \leq m \leq n - \lambda', \quad 1 \leq m' \leq n' - \lambda'',$$

it is easily seen that $M$ must satisfy

$$2 \leq M \leq (n-\lambda) + (n'-\lambda').$$

Furthermore, the substitution of $m' = M - m$ into the second of Equation (2.16) shows that, for a given $M$,

$$M - (n'-\lambda') \leq m \leq M - 1.$$  \hspace{1cm} (2.18)

Combining this with the first of Equation (2.16) gives

$$a \equiv \text{Max} \{1, M-(n'-\lambda')\} \leq m \leq \text{Min} \{n-\lambda, M-1\} \equiv b$$  \hspace{1cm} (2.19)

Equation (2.14) may now be written

$$I_\lambda (\nu\nu' | R) = \sum_{M=2}^{n-\lambda+n'-\lambda'} \left[ \sum_{m=a}^{b} D(\nu | m) D(\nu' | M-m) \right]$$

$$\times \int_0^{R - \alpha r} e^{-\alpha r} r^{\lambda+\xi+\lambda'+M} dr$$  \hspace{1cm} (2.20)

By introducing the substitution $\rho = \alpha r$, this can be expressed in a very compact form,

$$I_\lambda (\nu\nu' | R) = \sum_M \sigma(\nu\nu' | M) \alpha \int_0^{\alpha R} e^{-\rho} \rho^{\lambda+\xi+\lambda'+M} d\rho$$  \hspace{1cm} (2.21)
The new coefficients introduced here are given by
\[
\sigma(\nu \nu' \mid M) \equiv \alpha \sum_{m=0}^{b} D(\nu \mid m) D(\nu' \mid M-m) .
\] (2.22)

The integral in Equation (2.21) may be recognized as the incomplete gamma function\(^{9}\)
\[
\gamma(c \mid x) \equiv \int_{0}^{x} t^{c-1} e^{-t} dt .
\] (2.23)

For \( c = N \), an integer, this has the simple form
\[
\gamma(N \mid x) = \Gamma(N) \left[ 1 - e^{-x} E(N-1 \mid x) \right]
\] (2.24)

where \( \Gamma(N) \) is the ordinary gamma function, and
\[
E(N-1 \mid x) = \sum_{j=0}^{N-1} \frac{x^j}{j!}
\] (2.25)

is a truncated series expansion of the exponential \( e^x \). Note that for finite \( N \),
\[
\lim_{x \to \infty} \gamma(N \mid x) = \Gamma(N)
\] (2.26)

Incorporating these results into Equation (2.21) gives
\[
I_{\lambda}(\nu \nu' \mid R) = \alpha \times \sum_{M} \sigma(\nu \nu' \mid M)(\lambda+\nu+\nu'+M)! \left[ 1 - e^{-x} E(\lambda+\nu+\nu'+M \mid \alpha R) \right]
\] (2.27)

The second integral in \( \gamma_{\lambda} \) is now easily evaluated. Employing the fact that
\[
\int_{R}^{\infty} = \int_{0}^{\infty} - \int_{0}^{R} ,
\]
one may write immediately,

\[ J_\lambda(\nu\nu' \mid R) = I_{-\lambda-1}(\nu\nu' \mid \infty) - I_{-\lambda-1}(\nu\nu' \mid R) . \] (2.28)

Using Equations (2.26) and (2.27), and cancelling the constant terms gives the result

\[ J_\lambda(\nu\nu' \mid R) = \alpha^{\lambda+1} \times \sum_M \sigma(\nu\nu' \mid M)(-\lambda-1+\ell+\ell'+M)! e^{-\alpha R} \]

\[ \times E(-\lambda-1+\ell+\ell'+M \mid \alpha R) \] (2.29)

When this is combined with Equations (2.11) and (2.27), one obtains

\[ R_{\lambda}(\nu\nu' \mid R) = (\alpha R)^{-\lambda} \sum_M \sigma(\nu\nu' \mid M)(\lambda+\ell+\ell'+M)! + (\alpha R)^{\lambda+1} e^{-\alpha R} \]

\[ \times \sum_M \sigma(\nu\nu' \mid M) \left[ (-\lambda-1+\ell+\ell'+M)! E(-\lambda-1+\ell+\ell'+M \mid \alpha R) \right. \]

\[ - (\alpha R)^{-2\lambda-1} (\lambda+\ell+\ell'+M)! E(\lambda+\ell+\ell'+M \mid \alpha R) \] (2.30)

Two simplifications may be made in this expression to save computational effort. First, the multipole coefficient needs to be calculated only once,

\[ \tau_\lambda(\nu\nu') \equiv \sum_{M=2}^{n-\ell+\ell'-\ell'} \sigma(\nu\nu' \mid M)(\lambda+\ell+\ell'+M)! \] (2.31)

Second, one may note that for a given \( M \) term in the large summation, the last terms of the two \( E \) functions exactly cancel; i.e.,
\[
\frac{-\lambda - 1 + \ell + \ell' + M}{(-\lambda - 1 + \ell + \ell' + M)!} \frac{(\alpha R)}{(\alpha R)} \frac{-2\lambda - 1}{(\lambda + \ell + \ell' + M)!} \\
\times \frac{\lambda + \ell + \ell' + M}{(\lambda + \ell + \ell' + M)!} \equiv 0
\]

(2.32)

Thus, the order of each of the truncated exponentials may be lowered
by one. The final working equation is then

\[
R_{\lambda}^{\alpha}(\nu \nu' | R) = \tau_{\lambda}^{\alpha}(\nu \nu' )/(\alpha R)^{\lambda} + (\alpha R)^{\lambda + 1} - (\alpha R)^{\lambda + 1} \exp
\]

\[
\times \sum_{M} \sigma(\nu \nu' | M)[(-\lambda - 1 + \ell + \ell' + M)! E(-\lambda - 2 + \ell + \ell' + M | \alpha R)]
\]

\[
-2\lambda - 1
\]

\[
- (\alpha R)^{\lambda + 1} \omega(\lambda + \ell + \ell' + M)! E(\lambda - 1 + \ell + \ell' + M | \alpha R)]
\]

(2.33)

An important point when calculating the direct potential is the
following. For the diagonal terms,

\[
V_{L}(\nu \nu | R) = -2/R + \sum_{\ell} 2\ell_{\lambda}(\nu \nu ; L) y_{\lambda}(\nu \nu | R).
\]

(2.34)

For any \( \nu \), it is true that \( f_{0}(\nu \nu ; L) \tau_{0}(\nu \nu) = 1 \), and thus the \( R^{-1} \) drops
out. To see that \( \tau_{0}(\nu \nu) = 1 \), it is only required to look at the
normalization integral in Equation (2.9); then, using Equations (2.12),
(2.27), and (2.31) in that order,

\[
\int_{0}^{\infty} |P(\nu | r)|^2 dr = I_{0}(\nu \nu | \infty)
\]

\[
= \sum_{M} \sigma(\nu \nu | M)(\ell + \ell' + M)! \]

\[
= \tau_{0}(\nu \nu)
\]
Since \( f_0(\nu\nu'|R) \) is always unity (it is the normalization integral of the coupled angular basis; see Equation (2.40)), the practical conclusion is that the \( R^{-1} \) term in \( \psi_L \) may be simply ignored and never calculated.

The evaluation of Equation (2.33) can be accomplished as follows. First, set

\[
y_{\lambda}(\nu\nu'|R) = \tau_{\lambda}(\nu\nu')/(\alpha R)^\lambda.
\]  

(2.35)

Then, if \((\alpha R)\) does not exceed the cutoff parameter value, define the quantities

\[
\begin{align*}
f_a(1) &= (-\lambda+\ell+\ell')!, & f_b(1) &= (\lambda+\ell+\ell'+1)!, \\
E_a(2) &= E(-\lambda+\ell+\ell'|\alpha R), & E_b(2) &= E(\lambda+\ell+\ell'+1|\alpha R), \\
X_a(2) &= (\alpha R)^{-\lambda+\ell+\ell'} f_a(1), & X_b(2) &= (\alpha R)^{\lambda+\ell+\ell'+1} f_b(1), \\
2\lambda+1 &= h = R
\end{align*}
\]  

(2.36)

Note that \( X_a(2) \) and \( X_b(2) \) are simply the last terms to be added in the computation of \( E_a(2) \) and \( E_b(2) \), respectively. One now accumulates the summation

\[
S = \sum_{M=2}^{n-\ell+n'-\ell'} \sigma(\nu\nu'|M)[f_a(M) E_a(M) - f_b(M) E_b(M)/h],
\]  

(2.37)

where the various quantities are given by the recursion relations
\[
\begin{align*}
  f_a^a(M) &= (-\lambda-1+\alpha+\lambda'+M) f_a^a(M-1), \\
  f_b^a(M) &= (\lambda+\alpha+\lambda'+M) t_b^b(M-1), \\
  X_a^a(M) &= X_a^a(M-1) - (\lambda-1+\alpha+\lambda'+M) \\
  X_b^a(M) &= X_b^b(M-1) + (\lambda+\alpha+\lambda'+M) \\
  E_a^a(M) &= E_a^a(M-1) + X_a^a(M), \\
  E_b^a(M) &= E_b^b(M-1) - X_b^b(M)
\end{align*}
\]

Finally,
\[
y^\lambda_{VV'}(R) = R^{-\lambda} [y^\lambda_{VV'}(R) + (\alpha R)^{-\lambda}] e^S
\]

We note the symmetry with respect to interchange of \(v\) and \(v'\). Thus, only half of the off diagonal quantities, in particular, only the upper triangular half of the \(\sigma\) and \(\tau\) coefficients for each \(\lambda\), need be calculated and stored.

The algorithm given above was checked by means of hand calculation directly from Equation (2.33). The only checking with external sources was done with the short list of values given by Ormonde and Dick. In our opinion, the derivation given here is simpler than theirs, and is just as easy to evaluate. Also, our routine gave the exact results in every case.

**Angular Momentum Coupling Coefficients**

In the course of reducing the Hartree-Fock equations for the system, there arise matrix elements of the Legendre polynomial \(P_\lambda^{(\ell_1, \ell_2)}\) between states in the coupled representation. These matrix elements are

\[
f^\lambda_{VV'}(L) = \langle \ell_1, \ell_2 | P_\lambda^{(\ell_1, \ell_2)} | \ell_1', \ell_2' \rangle
\]
\[ g_\lambda (\nu' \nu ; L S) = (-1)^{(1-S)} \left( \ell_1 + \ell_2 - L \right) \langle \ell_1 \ell_2 L | P_\lambda | \ell_2' \ell_1' L \rangle. \quad (2.41) \]

These are computed from the general form given in Edmonds\textsuperscript{11}

\[ \langle \ell_a \ell_b L | P_\lambda | \ell_c \ell_d L \rangle = (-1)^{\ell_b + \ell_d + L} \]
\[ \times \left\{ \begin{array}{ccc}
\ell_b & \ell_a \\
\lambda & \ell_c & \ell_d \\
\end{array} \right\} \left[ \frac{(2\ell_a+1)(2\ell_b+1)(2\ell_c+1)(2\ell_d+1)}{12} \right] \]
\[ \times \left( \begin{array}{ccc}
\ell_a & \lambda & \ell_c \\
0 & 0 & 0 \\
\ell_b & \lambda & \ell_d \\
0 & 0 & 0 \\
\end{array} \right), \quad (2.42) \]

The quantity in large braces is a 6 - j coefficient, a formula for which is

\[ \begin{array}{c}
\left\{ \begin{array}{ccc}
j_1 & j_2 & j_3 \\
\ell_1 & \ell_2 & \ell_3 \\
\end{array} \right\} = \Delta(j_1 j_2 j_3) \Delta(j_1 \ell_2 \ell_3) \Delta(j_1 j_2 \ell_3) \Delta(\ell_1 \ell_2 j_3) \\
\times \omega\left( \begin{array}{ccc}
j_1 & j_2 & j_3 \\
\ell_1 & \ell_2 & \ell_3 \\
\end{array} \right), \quad (2.43) \end{array} \]

where the auxiliary functions are defined by

\[ \Delta(abc) = [(a+b-c)! (a-b+c)! (-a+b+c)!/(a+b+c+1)!] \quad (2.44) \]

\[ (= 0 \text{ if any factorial has a negative argument}) \]

and

\[ \omega\left( \begin{array}{ccc}
j_1 & j_2 & j_3 \\
\ell_1 & \ell_2 & \ell_3 \\
\end{array} \right) = \sum_z (-1)^z \frac{z(z+1)!}{D(j_1 j_2 j_3 \ell_1 \ell_2 \ell_3 | z)}, \quad (2.45) \]

\[ D(j_1 j_2 j_3 \ell_1 \ell_2 \ell_3 | z) = (z-j_1-j_2-j_3)! (z-j_1-j_2-\ell_3)! (z-\ell_1-j_2-\ell_3)! \\
(z-\ell_1-\ell_2-j_3)! (j_1+j_2+\ell_1+\ell_2-z)! \\
(j_2+j_3+\ell_2+\ell_3-z)! (j_3+j_1+\ell_3+\ell_1-z)! \quad (2.46) \]
The sum extends over those \( z \) for which no factorial has a negative argument.

In the large parentheses in Equation (2.42) are special forms of the 3-\( j \) coefficient. These may be calculated from

\[
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  0 & 0 & 0
\end{pmatrix}
= (-1)^{\frac{J}{2}} \frac{\left( \frac{1}{2} \right)!}{(\frac{1}{2} - j_1)! (\frac{1}{2} - j_2)! (\frac{1}{2} - j_3)!}
\]

\[
\times \frac{(J - 2j_1)! (J - 2j_2)! (J - 2j_3)!}{(\frac{1}{2} + j_1 + j_2 + j_3) \times (2j_1 + 1)! (2j_2 + 1)! (2j_3 + 1)!}
\]

(2.47)

where \( J = j_1 + j_2 + j_3 \) and must be even.

An examination of the restrictions involved in the preceding formulas shows that for a given \( \nu, \nu' \) pair, the allowed \( \lambda \) values in \( f_\lambda \) are

\[
\text{Max} \left\{ |\ell_2' - \ell_2|, |\ell_1' - \ell_1| \right\} \leq \lambda \leq \text{Min} \left\{ \ell_1 + \ell_1', \ell_2 + \ell_2' \right\}
\]

(2.48)

and in \( g_\lambda \)

\[
\text{Max} \left\{ |\ell_1' - \ell_2|, |\ell_1 - \ell_2'| \right\} \leq \lambda \leq \text{Min} \left\{ \ell_1' + \ell_2, \ell_1 + \ell_2' \right\}
\]

(2.49)

When the required \( f_\lambda \) and \( g_\lambda \) coefficients were computed, they were multiplied by two before they were stored. Also, because of the symmetry

\[
f_\lambda(\nu\mu;L) = f_\lambda(\mu\nu;L)
\]

(2.50)

only the upper triangular half (\( \mu \geq \nu \)) was stored for each \( \lambda \) value.

It will be recalled from Chapter Two that the first \( N_\nu \) sets of coupled equations are described by a single "incident channel" index \( \nu \),
but that the other $N_\xi$ sets require the triple $\xi = \{\nu \mu \lambda\}$. From
Equation (6) of that Chapter, it is evident that the required triplets
are just those for which $g_\lambda(\nu \mu ; L S)$ is non-zero. It is important to
note that $\mu$ and $\nu$ cannot be interchanged in $\xi$ without specifying a
different exchange term. Thus, the full set of required triplets will
be those corresponding to all of the non-zero $g_\lambda$, not just the upper
triangular set which was stored.

The $H(\nu \mu \lambda | R)$ Function

The function

$$H(\nu \mu \lambda | R) = G(\nu | R) H_a(\nu \mu \lambda | R) - F(\nu | R) H_b(\nu \mu \lambda | R),$$

(2.51)

where

$$H_a(\nu \mu \lambda | R) = \int_0^R F(\nu | r) P(\mu | r) r^\lambda \, dr,$$

(2.52)

$$H_b(\nu \mu \lambda | R) = \int_0^R G(\nu | r) P(\mu | r) r^{-\lambda-1} \, dr,$$

(2.53)

could be developed into a general formula like Equation (2.33). However,
the result is so complex that it is not worth the effort required, just
to get exact values of the function. Therefore, it was decided to
integrate the $H_a$ and $H_b$ functions numerically along with the integration
of the scattering equations. By using the same integration scheme,
and having exact values of the integrands, results at least as accurate
as the scattering functions (and probably more so) could be expected.
When exchange terms were dropped from the integration, the $H_a$ and $H_b$
were not further integrated, but treated from then on as constant
multipliers of $G(\nu | R)$ and $F(\nu | R)$. 
FÖRTRAN Computer Program

A FÖRTRAN program was written to perform the computations for this project in double precision on an IBM 7094 computer. A complete listing of the decks is contained in the Appendix. Figure 1 illustrates very schematically the design of the program. Some details of each block in the diagram are discussed in the following paragraphs. The discussions are keyed to the program through the use of program variable names.

Data Input

The program was designed to require a minimum amount of data for running a calculation. It first reads a run card with a run parameter and two control variables. The scattering state is then specified by the angular momentum LL, spin LS, and parity IPAR. Only channels for which \( \ell_1 + \ell_2 - L \) has the same parity as LL+IPAR will be constructed.

Another control variable, JEXCH, indicates whether or not exchange terms are to be included in the calculation. The energy of the system, with the convention that the hydrogen ground state has \( E = -1 \), is read into ENERGY. The atomic basis \( n \) and \( \ell_1 \) quantum numbers are read in, and if parity allows scattering channels for that state, the pair are stored in NBASIS and LBASIS.

The number of steps and step size in each integration region are read into NSTEP and DELTA. Also, \( R_N \) values, where output is to be generated, are read into RSAVE. Finally, the cutoff parameters are input. Exchange is cutoff for \( R > RCX \), while the exponential terms in the potential are cutoff for \( (R/n) > RCP \). In practice, these two cutoffs were always given the same value.
Figure 1

Schematic illustration of program design and operation.
Problem Setup

The scattering channels are defined by giving the n, $l_1$, and $l_2$ quantum numbers for each $\nu$. The method used to do this in the program is to take the arrays describing the atomic basis (n and $l_1$ values), develop arrays describing the required Ricatti-Bessel functions ($k_n$ and $l_2$ values), and then create labelling arrays which map a channel index $\nu$ onto the appropriate basis function descriptors and Bessel function descriptors. This procedure may be summarized in four steps.

1) From NBASIS and LBASIS take all $l_1$ values for a given n.
2) The possible partial waves at that energy $E_n$ for each $l_1$ lie between $l_2 = |L-l_1|$ and $(L+l_1)$. Determine the maximum and minimum $l_2$ for this $E_n$. Make parity corrections if necessary.
3) List ($k_n$, $l_2$) pairs in WBES and LBES. Enter all $l_2$ values between the minimum and maximum. If there are more than two, calculate the recursion factor and store in RBES.
4) Make label arrays such that $I = \text{LABELR} (\nu)$ is the index to be used in NBASIS and LBASIS to get the n and $l_1$ values for channel $\nu$, and $J = \text{LABELB} (\nu)$ is the index to be used in WBES and LBES to get the $k_n$ and $l_2$ values for channel $\nu$.
5) Repeat the above procedure for each n value.

Coefficient Calculation

Having at hand now the arrays describing the channels in the calculation, the program next calculates the arrays of constants needed
for the computation. This includes the \( D(\nu|m) \) coefficients for the
calculation of the associated Laguerre functions, the \( a(\nu\mu\lambda) \) energy
coefficients, the sets of \( \sigma(\nu\nu'|M) \) and \( \tau_{\lambda}(\nu\nu') \) coefficients for
calculating the direct potential, and the angular momentum coefficients
\( f_{\lambda}(\nu\nu';L) \) and \( g_{\lambda}(\nu\nu';LS) \). These are stored respectively in the arrays
\( D, AC, SIGMA, TAU, FC, \) and \( GC \). Note that all index calculation is
done by the program itself so that all arrays are referenced as
singly subscripted vectors. The advantages are two-fold. First, this
allows upper-triangular storage of symmetric matrices to save core
storage. Second, quicker reference can be achieved when the arrays
are used in summation loops.

Two other important arrays are created in this section. The first
is \( \text{INDIC} \), a mapping of the non-zero \( f_{\lambda} \) coefficients onto \( (n,l_1)(n',l'_1) \)
pairs. This provides the function routine with the knowledge of
which \( y_{\lambda}(\nu\nu'|R) \) will be multiplied by a non-zero \( f_{\lambda} \) and must be calculated.
If \( I \) is an index for basis functions, then the \( \text{INDIC} \) location associated
with \( (I,I',\lambda) \) is .TRUE. if the corresponding \( y_{\lambda} \) is not to be calculated.

From the non-zero \( g_{\lambda} \), a set of arrays, \( \text{NZETA}, \text{MZETA}, \) and \( \text{LZETA} \), are
constructed which contain the triplets \( (\nu\mu\lambda) \) for the \( \xi \) labels.

The last function of this section is to output all the pertinent
information about the run and its setup. A listing of the internal
arrays is optional.

**Integration Director and Integrator**

The structure of the scattering equations suggested a division of
labor along the following lines. Matrices are set up for all of the
radical functions \( F \), and all the integrals \( A, B, Q, \) and \( U \). Each
column of this set corresponds to the set of \( F, A, B, Q, \) and \( U \) which are generated when a particular one of the \( \phi \) functions is selected. An integrator was constructed which could "operate" on any column of these matrices. Given a column of \( F, A, B, Q, \) and \( U \) at \( R_i \) and values of all the known functions at \( R_{i+1} \), the integrator integrates the column one step forward according to the scheme described in Section 1 of this Chapter. The only modification from column to column is the use of a different \( \phi \).

The integrator is driven by the integration director. Its functions are to move to the next grid point, have the known functions evaluated there, and furnish these functions and the various \( N_Y + N_{\xi} \) columns of \( F, A, B, Q, \) and \( U \) matrices to the integrator, along with information about which \( \phi \) is to be used for each column.

Whenever the director increments the previous grid point and arrives at one of the \( R_N \), it temporarily interrupts the integration to call on the matrix generator routine and initiate calculation of the \( R \) matrix and cross sections for that \( R_N \).

Matrix Generator, Projector, and Output

The purpose of the matrix generator is to take the current values of the \( A, B, Q, \) and \( U \) integrals and the \( H_a \) and \( H_b \) "constants" and construct the matrices \( \mathbf{M} \) (Equation (39), Chapter Two) and \( \mathbf{E} \) (Equation (44), Chapter Two). The \( A^0 \) and \( \hat{A} \) integrals are stored in \( \text{ATEG} \); the \( B^0 \) and \( \hat{B} \) integrals are stored in \( \text{BTEMP} \). The \( \beta^0 \) and \( \beta^1 \) quantities are calculated and stored in \( \text{EXCH} \).

In order to calculate the \( R \) matrix and cross sections, the \( \text{BTEMP} \) and \( \text{EXCH} \) matrices are combined to form \( \mathbf{X} \), the program matrix corresponding
to M. This array, along with ATEMP (which corresponds to E), is passed to the output routine. In that routine, the R matrix and the real and imaginary parts of the T matrix are calculated and printed out. Cross sections are also calculated and printed out.

If the program control variable JPC has been set to zero to indicate the presence of the 2p state, the matrix generator calls for the approximate matricant, \( \Omega_1 \), to be computed and stored in T. This matrix is used to transform simultaneously the columns of ATEMP and BTEMP. The projected values are stored again in ATEMP and BTEMP. The operations in the preceding paragraph are then repeated.

Control is finally passed back to the integration director.
REFERENCES


APPENDIX

The electron scattering program described in the last Section of this Chapter is composed of the routines in the following list. All subroutine deck names begin with "S" and all function deck names begin with "F".

<table>
<thead>
<tr>
<th>DECK</th>
<th>ROUTINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. MAIN</td>
<td>main program</td>
</tr>
<tr>
<td>2. BLKD</td>
<td>BLOCK DATA</td>
</tr>
<tr>
<td>3. SDAT</td>
<td>DATE</td>
</tr>
<tr>
<td>4. SFFS</td>
<td>FFSTR</td>
</tr>
<tr>
<td>5. SINT</td>
<td>INTSYS</td>
</tr>
<tr>
<td>6. SSAV</td>
<td>SAVINT</td>
</tr>
<tr>
<td>7. SOUT</td>
<td>OUTPUT</td>
</tr>
<tr>
<td>8. SSIM</td>
<td>SIMUL</td>
</tr>
<tr>
<td>9. STFM</td>
<td>TFMN</td>
</tr>
<tr>
<td>10. SCON</td>
<td>CONST</td>
</tr>
<tr>
<td>11. STRI</td>
<td>TRIG</td>
</tr>
<tr>
<td>12. SGRE</td>
<td>GREENS</td>
</tr>
<tr>
<td>13. FTRU</td>
<td>TRUNCX</td>
</tr>
<tr>
<td>14. FFAC</td>
<td>FACT</td>
</tr>
<tr>
<td>15. FPLJ</td>
<td>PLJ</td>
</tr>
<tr>
<td>16. FC6J</td>
<td>C6J</td>
</tr>
<tr>
<td>17. FSPC</td>
<td>SPC3J</td>
</tr>
<tr>
<td>18. FDEL</td>
<td>DELT</td>
</tr>
<tr>
<td>19. FDFL</td>
<td>DFLOAT</td>
</tr>
<tr>
<td>20. SLIS</td>
<td>LIST</td>
</tr>
<tr>
<td>21. SFFL</td>
<td>FFLIST</td>
</tr>
</tbody>
</table>

The purpose of each routine is indicated in the commentary there. Equation numbers refer back to Chapter Four.
C MAIN PROGRAM DECK, VERSION 7.0, 08/16/71.
C
C DIMENSION WORD(8)
C DATA WORD / 6HSING, 6HTRIP, 6HOPEN, 6HCLOSED, 
C * 6HIX, 6HIN, 6HFILES, 6HLISTS /
C
C COMMON /IPLK/
C * NRUN, IPC, JPC, LL, LS, IPAR, JEXCH, NBASIS(3), LBASIS(3), 
C * LBES(4), JBES(4), LABEL(4), LABELB(4), INDIC(16), 
C * NZETA(18), WZETA(18), LZETA(18), NSTEP(2)
C COMMON /DBL/
C * WBES(41), RRES(41), D(6), AC(6), SIGMA(18), TAU(18), 
C * FC(30), GC(50), P(3), FBESE(4), GBESE(4), Y(18), V(16), 
C * HA(18), HJH(18), PHII(22), DELTA(2), RSAVE(20), RLST(6), 
C * R, DR, RCK, RCP, ENERGY
C COMMON /CNS/
C * NCHAN, NLAG, NBES, NMAX, NMAX2, LMAX, LMAX2, MMAX, MNG, MNG, MNG, 
C * NLIN, NLG, NMS, NZG, NTOTAL, NFILES, NLISTS, MFLE, MLIST
C COMMON /INT/
C * F(4,22), W(4,22), A(4,22), B(4,22), Q(18,22), U(18,22)
C COMMON /CONS/
C * ZERD, ONE, TWO
C
C LOGICAL INDIC
C
C DOUBLE PRECISION
C * WBES, RRES, D, AC, SIGMA, TAU, FC, GC, P, FBESE, GBESE, Y, V, 
C * HA, HA, PHI, DELTA, RSAVE, RLST, R, DR, RCK, RCP, ENERGY
C * F, W, A, B, Q, U, ZERD, ONE, TWO, ENDPT,
C * FACT, PLJ, DFLQ, DTEMP, DTEMP, GTEMP, MTHOL
C
C 100 FORMAT (1H1//6H DATE**, 2X, 12, 1H, /12, 1H, /12, 90X, 8H VERSION, *, A6//)
C 101 FORMAT (10I5)
C 102 FORMAT (5D16.0)
C 103 FORMAT (22I3)
C 104 FORMAT (35X, 4H DESCRIPTION OF CHANNELS IN THIS CALCULATION, /
C * // 20H STATE SPECIFICATION, 9X, 18HANGULAR MOMENTUM = 13, 
C * 17H SPIN STATE = 0A4, 15HLET, PARITY = 12, 1H, 
C * // 23H TOTAL ENERGY OF SYSTEM, 6X, F7.4, 10H RYDBERGS, 
C * // 15H CHANNEL MATRIX, 1X, 7CHannel, 2X, 1HN, 3X, 2MIL, 3X, 
C * 2HL, 5X, 6HLABELR, 3X, 6H_LABELB /)
C 105 FORMAT (30X, 1H4, 12, 1H, 315, 219, 8X, A6)
C 106 FORMAT (//2H LAGUERRE DESCRIPTORS, 8X, 6H_LABELR, 3X, 1HN, 4X, 1H/)
C 107 FORMAT (19H BESSEL DESCRIPTORS, 10X, 6H_LABELB, 6X, 4H_BESSE, 7X, 
C * 4MILBES, 6X, 4HRES /)
C 108 FORMAT (30X, 1H4, 12, 1H, 6X, F7.5, 6X, 12, 6X, F7.5, 7X, A6)
C 109 FORMAT (//15H EXCHANGE TERMS, 14X, A2, 7HIMPLIED, /)
C 110 FORMAT (//23H INTEGRATION PARAMETERS, 6X, 6REGION, 3X, 
C * 12HND. OF STEPS, 3X, 9STEP SIZE, 7X, 9RANGE, /
C * 30X, 3HONE, 7X, I4, 12X, F6.4, 7X, FR, 4, /
C * 30X, 3HMTO, 7X, I4, 12X, F6.4, 7X, FR, 4 /)
C 111 FORMAT (//8H OUTPUT, A5, 16X, 5I12, 1H, =, F8.4, 3X,1/
C * (29X, 5I12, 1H, =, F8.4, 3X)))
C 112 FORMAT (1H4H CUTOFF VALUES, 15X, 6HRCX, =, F8.4, 9H, RCP, =, F8.4, 155 /
C * (15H ELAPSED TIME, 9H, 3, 9H SECONDS.)
C
C ASSIGN VERSION NUMBER OF PROGRAM TO NVER.
C DATA NVER / 4H, 7.0 /
C
C CALL DATE (IDATE, JDATE, KDATE)
C 1000 CALL SETIME
C
C *************
C * DATA INPUT *
C *************
C
C READ (5,101) NRUN, IPC, JPC
C
NRUN IS AN EXIT PARAMETER, IPC IS A CONTROL FOR PRINTING
C
INTERNAL ARRAYS, AND JPC IS A CONTROL FOR APPLYING THE
C
PROJECTION PROCEDURE.
C
IF (NRUN.EQ.0) CALL EXIT
C
WRITE (6,100) IDATE, JDAT, KDATE, NVER
C
INPUT SPECIFICATIONS OF STATE.
C
READ (5,101) LL, LS, IPAR, JEXCH
READ (5,102) ENERGY
C
INITIALIZE QUANTUM NUMBERS AND COUNTERS.
C
NMAX = 0
C
LMAX = 0
C
NL = 0
C
NCHAN = 0
C
INPUT THE H - ATOM BASIS STATES.
C
1005 READ (5,101) N, L
C
TERMINATE BASIS STATE INPUT WITH A N=0 CARD.
C
IF (N.EQ.0) GO TO 1015
C
CALCULATE MAXIMUM AND MINIMUM PARTIAL WAVES.
C
I = IABS(LL-L)
J = LL+L
C
CHECK PARITY RESTRICTION.
C
IF (IPAR.EQ.0) GO TO 1010
I = I+1
J = J-1
C
CALCULATE NUMBER OF CHANNELS GENERATED BY THIS STATE.
C
1010 M = 1+J-I/2
C
IGNORE THIS STATE IF M IS ZERO.
C
IF (M.EQ.0) GO TO 1005
C
STORE THIS BASIS STATE.
C
NL = NLAG+1
NH = J(NLAG) = N
LH = L(NLAG) = L
C
COUNT NUMBER OF CHANNELS.
C
NCHAN = NCHAN+M
C
FIND LARGEST N AND L QUANTUM NUMBERS.
C
IF (NH.GT.NMAX) NMAX = NH
IF (LH.GT.LMAX) LMAX = LH
C
GO BACK TO PICK UP NEXT BASIS STATE.
C
1005 TO 1005
C
MISCELLANEOUS QUANTITIES.
C
1015 NMAX = 2*NMAX
LMAX = 2*LMAX
MXG = LL+LMAX
MNG = MAX(0,LL-LMAX)
MNG = MNG-1
NL = LMAX+1
NLG = MXG-MNG
NMS = NMAX+1
C
INPUT REMAINING CARDS.
C
READ (5,101) NSTEP(1), NSTEP(2)
READ (5,102) DELTA(1), DELTA(2)
READ (5,101) NFILES
IF (NFILES.GT.0) READ (5,102) (RSAVE(MFILE), MFILE=1,NFILES)
READ (5,101) NLISTS
IF (NLISTS.GT.0) READ (5,102) (RLIST(MLIST), MLIST=1,NLISTS)
READ (5,102) RCX, RCP
**PROBLEM SETUP**

**THIS SECTION MAKES CHANNEL MATRIX, LABEL ARRAYS, AND BESSEL DESCRIPTOR ARRAYS.**

```plaintext
IPLUS = 1
JPLUS = 1
NBES = 0
IOF = 1
JOF = 1

C INITIALIZE UPPER AND LOWER PARTIAL WAVE BOUNDS FOR THIS N.
1020 JTEMP = 0
ITEMP = LL+LMAX
C PICK UP BASIS STATE.
N = NBASIS(IPLUS)
1029 L = LBASIS(IPLUS)
C CALCULATE MAXIMUM AND MINIMUM PARTIAL WAVES FOR THIS STATE.
I = IARS(LL-L)
J = LL+L
C PARITY CORRECTION.
IF (1PAR,EQ,3) GO TO 1030
I = I+1
J = J-1
C FIND MAXIMUM AND MINIMUM PARTIAL WAVE VALUES FOR THIS N.
1030 IF (I.LT.JTEMP) ITEM = I
IF (J.GT.JTEMP) JTEM = J
C MAKE LABEL FOR RADIAL FUNCTIONS, TEMPORARILY STORE PARTIAL WAVE VALUES IN BESSEL LABEL ARRAY.
1035 LABEL(I,JDF) = IPLUS
LABEL(J,JDF) = I
JOF = JOF+1
IF (1.EQ,J) GO TO 1040
I = I+2
GO TO 1035
C ADVANCE BASIS STATE COUNTER.
1040 IPLUS = IPLUS+1
C HAS LAST BASIS STATE BEEN CONSIDERED?
IF (IPLUS.GT.NLAG) GO TO 1045
C NEXT N DIFFERENT.
IF (NBASIS(IPLUS),EQ,N) GO TO 1025
C CONVERT PARTIAL WAVE VALUES TO LABELS.
1045 M = JPLUS-JTEMP
1050 LABEL(I,JDF) = LABEL(I,JDF)+M
IOF = IOF+1
IF (IOF.LT.JOF) GO TO 1050
JPLUS = JTEMP+M+1
C CALCULATE ENERGY FOR THIS GROUP OF CHANNELS. ATOMIC GROUND STATE HAS E=-1.00
DTEMP = ENERGY+ONE/DFLOAT(N**2)
C IS CHANNEL OPEN OR CLOSED.
M = 0
IF (DTEMP.GT.ZERO) GO TO 1055
DTEMP = -DTEMP
M = 1
C CALCULATE WAVE NUMBER FOR CHANNELS.
1055 DTEMP = DSQRT(DTEMP)
C MAKE UP BESSEL DESCRIPTORS FOR THIS GROUP OF CHANNELS.
N = NBES
```

MAIN 145
MAIN 146
MAIN 147
MAIN 148
MAIN 149
MAIN 150
MAIN 151
MAIN 152
MAIN 153
MAIN 154
MAIN 155
MAIN 156
MAIN 157
MAIN 158
MAIN 159
MAIN 160
MAIN 161
MAIN 162
MAIN 163
MAIN 164
MAIN 165
MAIN 166
MAIN 167
MAIN 168
MAIN 169
MAIN 170
MAIN 171
MAIN 172
MAIN 173
MAIN 174
MAIN 175
MAIN 176
MAIN 177
MAIN 178
MAIN 179
MAIN 180
MAIN 181
MAIN 182
MAIN 183
MAIN 184
MAIN 185
MAIN 186
MAIN 187
MAIN 188
MAIN 189
MAIN 190
MAIN 191
MAIN 192
MAIN 193
MAIN 194
MAIN 195
MAIN 196
MAIN 197
MAIN 198
MAIN 199
MAIN 200
MAIN 201
MAIN 202
MAIN 203
MAIN 204
MAIN 205
MAIN 206
MAIN 207
MAIN 208
MAIN 209
MAIN 210
MAIN 211
MAIN 212
MAIN 213
MAIN 214
MAIN 215
MAIN 216
MAIN 217
MAIN 218
MAIN 219
301

1060 NBES = NBES+1
1061 VBES(NBES) = DTEMP
1062 LBES(NBES) = ITEMP
1063 KBES(NBES) = DFLOAT(2*ITEMP-1)/DTEMP
1064 JBES(NBES) = M
1065 IF (ITEMP,EQ., JTEMP) GO TO 1065
1066 ITEMP = ITEMP+1
1067 GO TO 1060

C C SET TO ZERO FIRST (AND SECOND) RECURSION FACTORS OF A STRING.
1065 L = MIND(NBES,N+2)
1070 N = N+1
1071 NBES(N) = ZERO
1072 IF (N,LT,L) GO TO 1070

C C HAS LAST N - GROUP BEEN ACCOUNTED FOR.
1073 IF (IPLJS.EQ.,NLAG) GO TO 1075

C C IF NOT, RETURN TO NEXT N - GROUP.
1074 GO TO 1020

C C

*******************************************************************
C C * COEFFICIENT CALCULATION *

*******************************************************************

C C THIS SECTION CALCULATES THE D, AC, SIGMA, TAU, FC, AND GC
C C COEFFICIENTS. IT ALSO CONSTRUCTS THE INDIC ARRAY AND THRE
C C ZETA DESCRIPTORS.

C C CALCULATION OF D AND AC COEFFICIENTS.

1075 ICOUNT = 0
1076 I = 0
1085 ICOUNT = ICOUNT+1
1086 IPLJS = I+1
1087 IDF = I*XMAX
1088 N = NBASIS(IPLUS)
1089 L = LBASIS(IPLUS)
1090 M = N-L
1095 J = J+1

C C GET STARTING VALUE FOR RECURSION, EQ. (2.88).

1090 DTEMP = DFLOAT(2**(L+1))*DSQRT(FACT(N+1)/FACT(N-L-1))
1091 * (DFLOAT(N**2*L+2)*FACT(K))

C C RECURSE ACCORDING TO EQ. (2.8A).

1095 J = J+1
1096 JTEMP = J+IDF
1097 DIJTEMP = DTEMP
1098 IF (J,EQ.,M) GO TO 1090
1099 DTEMP = DTEMP*DFLOAT(2*(J-M))/DFLOAT(J*XN*K+J)
1100 GO TO 1095

C C CALCULATE ENERGY COEFFICIENTS BETWEEN THIS AND ALL
C C EARLIER BASIS STATES, EQ. (2.10).

1105 ICOUNT = ICOUNT+1
1106 I = 0

C C CALCULATION OF SIGMA AND TAU COEFFICIENTS.

1100 ICOUNT = 0
1101 I = 0
1105 ICOUNT = ICOUNT+1
1106 IPLJS = I+1
1107 N1 = NBASIS(IPLUS)
1108 L1 = LBASIS(IPLUS)
NML1 = NI-L1
JOF = IT*NMAX
J = 0
1110 JPLUS = J+1
NJ = NABASIS(JPLUS)
LJ = LBASESIS(JPLUS)
NMLJ = NJ-LJ
JOF = J*NMAX
MLIM = NML1+NMLJ
MTEMP = (J+ICOUNT)*NMS-1
C
C CALCULATE RECIPROCAL ALPHA, EQ. (2.15).
FTEMP = DFRAT(I+NJ)/DFLOAT(I+J)
GTEMP = FTEMP**((LI+LJ+2)
M = 2
1115 GTEMP = GTEMP*FTEMP
N = MAXD(1,N-MMLJ)
L = MIND(N-1,NML1)
C
C FOR SIGMA, SUM PRODUCTS OF D COEFFICIENTS, EQ. (2.22).
DTEMP = ZERD
1120 ITEMP = N+JOF
JTEMP = M+JOF
DTEMP = DTEMP+DFLAT(ITEMP)*DJTEMP
IF (N.EQ.L) GO TO 1125
N = N+1
GO TO 1120
1125 K = M+MTEMP
SIGMA(K) = DTEMP*GTEMP
IF (M.EQ.MLIM) GO TO 1130
M = M+1
GO TO 1115
1130 LTEMP = (J+ICOUNT)*NLF+1
L = 0
1135 N = L+LI+LJ
FTEMP = FACT(N+1)
C
C FOR TAU, SUM SIGMA COEFFICIENTS, EQ. (2.31).
DTEMP = ZERD
1140 FTEMP = FTEMP*DFLAT(N*M)
K = M+MTEMP
DTEMP = DTEMP+SIGMA(K)*FTEMP
IF (M.EQ.MLIM) GO TO 1145
M = M+1
GO TO 1140
1145 K = L+LTEMP
TAU(K) = DTEMP
IF (L.EQ.LMAX) GO TO 1150
L = L+1
GO TO 1135
1150 IF (JPLUS.EQ.0) GO TO 1155
J = JPLUS
GO TO 1110
C
C FOR TAU ON I,J-DIAGONAL, L=0, SET TO ZERO.
1155 TAU(LTEMP) = ZERD
IF (IPLUS.EQ.NLAG) GO TO 1160
I = IPLUS
GO TO 1105
C
C CALCULATION OF FC AND GC COEFFICIENTS, Eqs. (2.40) AND (2.41).
C
C ROUTINE PLJ USED TO EVALUATE INTEGRAL IN EQ. (2.42).
1160 MTEMP = NLF*(NLAG*(MLIM+1))*2
DO 1165 M=1,MTEMP
INDIC(M) = .TRUE.
1165 CONTINUE
C
GTEMP = TWO
IF (LS.EQ.IPAR) GTEMP = -TWO
C
ICOUNT = 0
I = 0
1170 ICOUNT = ICOUNT+1
IPLUS = I+1
C
MAIN 294
MAIN 295
MAIN 296
MAIN 297
MAIN 298
MAIN 299
MAIN 300
MAIN 301
MAIN 302
MAIN 303
MAIN 304
MAIN 305
MAIN 306
MAIN 307
MAIN 308
MAIN 309
MAIN 310
MAIN 311
MAIN 312
MAIN 313
MAIN 314
MAIN 315
MAIN 316
MAIN 317
MAIN 318
MAIN 319
MAIN 320
MAIN 321
MAIN 322
MAIN 323
MAIN 324
MAIN 325
MAIN 326
MAIN 327
MAIN 328
MAIN 329
MAIN 330
MAIN 331
MAIN 332
MAIN 333
MAIN 334
MAIN 335
MAIN 336
MAIN 337
MAIN 338
MAIN 339
MAIN 340
MAIN 341
MAIN 342
MAIN 343
MAIN 344
MAIN 345
MAIN 346
MAIN 347
MAIN 348
MAIN 349
MAIN 350
MAIN 351
MAIN 352
MAIN 353
MAIN 354
MAIN 355
MAIN 356
MAIN 357
MAIN 358
MAIN 359
MAIN 360
MAIN 361
MAIN 362
MAIN 363
MAIN 364
MAIN 365
MAIN 366
MAIN 367
MAIN 368
IF (L+1)<LMAX2) GO TO 1190
L = L+1
GO TO 1180

C CALCULATION OF GC COEFFICIENTS.
1195 M = L+MTEMP
IF (L+1)<LMAX2) GO TO 1200
M = L+MTEMP
GO TO 1195

C MAKE ZETA DESCRIPTOR ARRAYS FOR NON-ZERO GC COEFFICIENTS.
1210 NZG = 0
IF (L+1)<LMAX2) GO TO 1255
1215 IPLUS = I+1
J = 0
1220 JPLUS = J+1
IF (LCG(JTEMP).EQ.0) GO TO 1225
ITEMP = (J+IPLUS)/2*NLG-MMG
GO TO 1230
1225 ITEMP = (I+JPLUS)/2*NLG-MMG

C NOW LIST ALL PERTINENT INFORMATION TO IDENTIFY RUN.
FTEMP = DELTA(1)+DIFLOAT(NSTEP(1))
GTEMP = DELTA(2)+DIFLOAT(NSTEP(2))
WRITE (6,104) LL, WORD(LS+1), IPAR, ENERGY
DO 1260 I=1,NCHAN
ITEMP = LABELR(I)
JTEMP = LABELL(I)
J = JBES(JTEMP)+3
WRITE (6,105) I, NBASIS(ITEMP), LBASIS(ITEMP), LBES(JTEMP), -ITEMP, JTEMP, WORD(J)
1260 CONTINUE
WRITE (6,106)
DO 1265 I=1,NLAG
WRITE (6,105) I, NBASIS(I), LBASIS(I)
1265 CONTINUE
WRITE (6,107)
DO 1270 I=1,NBES
J = JBES(I)+3
WRITE (6,108) I, WBES(I), LBES(I), RBES(I), WORD(J)
1270 CONTINUE
WRITE (6,109) WORD(JEXCH+5)
WRITE (6,110) NSTEP(1), DELTA(1), FTEMP, NSTEP(2), DELTA(2), GTEMP
IF (NLISTS.GT.0) WRITE (6,111) WORD(7), (I, RSAVE(I), I=1,NLISTS)
IF (NLISTS.GT.0) WRITE (6,111) WORD(8), (I, RLIST(I), I=1,NLISTS)
WRITE (6,112) RCK, RCP
C
C PRINT CONTROL SET TO 1 WILL LIST INTERNAL ARRAYS.
C IF (IPC.EQ.1) CALL LIST
C
C ************************************************************************
C **  INTEGRATION DIRECTOR  **
C ************************************************************************
C
C INITIALIZE ALL INTEGRALS TO ZERO.
DO 1285 J=1,NTOTAL
DO 1275 I=1,NCHAN
A(I,J) = ZERO
B(I,J) = ZERO
1275 CONTINUE
DO 1280 I=1,NZG
U(I,J) = ZERO
Q(I,J) = ZERO
1280 CONTINUE
1285 CONTINUE
DO 1290 J=1,NZG
HA(J) = ZERO
HB(J) = ZERO
1290 CONTINUE
C
C INTEGRATE THRU INNER REGION.
R = ZERO
NUMSTP = 0
DR = DELTA(1)
NS = NSTEP(1)
ENDPT = (DELTA(1)+DELTA(2))/TWO
C
1295 R = R+DR
NUMSTP = NUMSTP+1
IF (NUMSTP.EQ.NS) DR = ENDPT
C
C GET FUNCTIONS AT THIS POINT.
CALL FFSR
C
C LOOP THRU THE DIRECT ZETA SETS.
DO 1300 I=1,NCHAN
CALL INTSYS (F(I,1),W(I,1),A(I,1),B(I,1),Q(I,1),U(I,1),1,1)
1300 CONTINUE
C
C LOOP THRU THE EXCHANGE ZETA SETS.
IF (JEXCH.EQ.0) GO TO 1310
DO 1305 I=1,NZG
J = NZETA(I)
K = I*NCHAN
CALL INTSYS (F(I,K),W(I,K),A(I,K),B(I,K),Q(I,K),U(I,K),J,K)
1305 CONTINUE
C
1310 IF (NUMSTP.LT.NS) GO TO 1295
C
C INTEGRATE THRU THE OUTER REGION.
C
C IF (NFILES.EQ.0) GO TO 1315
C NSV = NSTEP(2)+1
C GO TO 1320
1315 MFILE = 1
C NSV = (RSAVE(MFILE)-RHOLD)/DELTA(2)
C
C 1320 IF (NLISTS.EQ.0) GO TO 1325
C LST = NSTEP(2)+1
C GO TO 1330
1325 MLIST = 1
C LST = (RLIST(MLIST)-RHOLD)/DELTA(2)
C
C 1330 NUMSTP = 0
C DR = DELTA(2)
C VS = NSTEP(2)
C EVNPT = DELTA(2)/TWO
C
C 1335 R = R+DR
C NUMSTP = NUMSTP+1
C IF (NUMSTP.EQ.NS) DR = EVNPT
C
C GET FUNCTIONS AT THIS POINT.
C CALL FFSTR
C
C LOOP THRU THE DIRECT ZETA SETS.
C DO 1340 I=1,NCHAN
C CALL INTSYS (F(1,I),W(1,I),A(1,I),B(1,I),Q(1,I),U(1,I),I,I)
C 1340 CONTINUE
C
C LOOP THRU THE EXCHANGE ZETA SETS.
C IF (JEXCH.EQ.0) GO TO 1350
C DO 1345 I=1,NZG
C J = NZETA(I)
C K = I+NCHAN
C CALL INTSYS (F(1,K),W(1,K),A(1,K),B(1,K),Q(1,K),U(1,K),J,K)
C 1345 CONTINUE
C
C 1350 IF (NUMSTP.LT.NSV) GO TO 1355
C C GIVE INTEGRALS TO MATRIX GENERATOR.
C CALL SAVINT
C
C IF (MFILE.EQ.NFILES) GO TO 1355
C MFILE = MFILE+1
C NSV = (RSAVE(MFILE)-RHOLD)/DELTA(2)
C
C 1355 IF (NUMSTP.LT.LST) GO TO 1360
C C LIST ARRAYS.
C CALL FFLIST
C
C IF (MLIST.EQ.NLISTS) GO TO 1360
C MLIST = MLIST+1
C LST = (RLIST(MLIST)-RHOLD)/DELTA(2)
C 1360 IF (NUMSTP.LT.NS) GO TO 1335
C
C CALL GETIME (TEMP)
C TEMP = TEMP/60.
C WRITE (6,115) TEMP
C GO TO 1000
C END
BLOCK DATA

ASSIGN COMMONLY USED DOUBLE PRECISION CONSTANTS.

COMMON /CONS/
    ZERO, ONE, TWO
DATA ZERO, ONE, TWO / 0.0D0, 1.0D0, 2.0D0 /

END

SUBROUTINE DATE (II, JJ, KK)

THIS ROUTINE GETS THE RGD WORD (MMDDYY) AND RETURNS THE INTEGERS II, JJ, KK, WHERE II=MTH, JJ=DAY, KK=YEAR.

IDIV = 64
CALL JDAT1 (M)
N = M/IDIV
KK = N/IDIV
M = N/IDIV
JJ = JJ+10*(N-IDIV*M)
II = M-IDIV*
N = N/IDIV
II = II+10*(N-IDIV*M)
RETURN
END

SUBROUTINE FFSTR

THIS ROUTINE EVALUATES THE KNOWN FUNCTIONS AT THE CURRENT VALUE OF THE COORDINATE R.

COMMON /BLK/
    MKRN, IPC, JPC, LL, LS, IPAR, JEXCH, NBASIS(3), LBASIS(3),
    LBSI(4), JBSI(4), LABEL(4), LABELD(4), INDIC(18),
    NZETA(10), NETA(10), LETA(10), NSTEP(2)
COMMON /DLK/
    WWII(4), JBSI(4), DI(6), AC(6), SIGMA(18), TAU(18),
    FC(30), GC(30), P(3), FBESL(4), GBESL(4), Y(18), V(16),
    HAI(18), HHI(18), PHI(22), DELTA(2), RSAVE(201), RLIST(6),
    R, DR, RCK, RCP, ENERGY
COMMON /CNTS/
    NCHAN, NLG, NBES, NMAX, NMAX2, LMAX, LMAX2, MNG, MNG2, MXG,
    NLF, NLG, NMS, NZG, NTOTAL, NFIL, NFILS, NFILS, NFILS, MLIST
COMMON /COVS/
    ZER, ONE, TWO

LOGICAL INDC

DOUBLE PRECISION
    WB, WBS, RBS, D, AC, SIGMA, TAU, FC, GC, P, FBESL, GBESL, Y, V,
    HA, HD, PHI, DELTA, RSAVE, RLIST, R, RCK, RCP, ZER, ONE, TWO,
    DTEM, DTEM, DTEM, DTEM, ALPHER, FAC1, FAC2, E1, E2,
    X1, X2, D1, D2, DFLOAT, FACT, TRUNCX, DR, ENERGY

IF (JEXCH.EQ.0) GO TO 1020
IF (R.GT.RCK) GO TO 1020
C CALCULATE RADIAL FUNCTIONS, EQU. (2.7).
I = 0
1005 IPLUS = I+1
IOF = I*NMAX
N = NBASIS(IPLUS)
L = LBASIS(IPLUS)
M = N-L
GTEMP = ZERO
FTEMP = R
J = 1
1010 K = J+IOF
GTEMP = GTEMP+D(K)*FTEMP
IF (J.EQ.M) GO TO 1019
J = J+1
FTEMP = FTEMP*R
GO TO 1010
1015 PIPLUS) = (R**L)*GTEMP*DEXP(-R/DFLOAT(N))
IF (IPLUS.NE.NLAG) GO TO 1020
I = IPLUS
GO TO 1005
C C CALCULATE HESSIAN FUNCTIONS, ROUTINE GREENS IS USED TO
C EVALUATE EOS. (2.2A) AND (2.2B).
C
1020 I = 1
1025 IF (RBE5(I).EQ.ZERO) GO TO 1030
FTEMP = RBES(I)/R
FBESL(I) = FTEMP*FBESL(I-1)-FBESL(I-2)
GHESL(I) = FTEMP*GHESL(I-1)-GHESL(I-2)
GO TO 1035
1030 CALL GREENS (FBESL(I),GHESL(I),LBESL(I),R)
1035 IF (I.EQ.NBES) GO TO 1040
I = I+1
GO TO 1025
C C CALCULATE Y FUNCTIONS, EQU. (2.11).
1040 ICOUNT = 0
1045 ICOUNT = ICOUNT+I
IPLUS = I+1
NI = NBASIS(IPLUS)
J = 0
1050 JPLUS = J+1
NJ = NBASIS(JPLUS)
NLPLUS = NI*NJ
LPLUS = LBASIS(IPLUS)*LBASIS(JPLUS)
ALPHAR = R/DFLOAT(NLPLUS)*DFLOAT(NI+NJ)
C
LTEMP = (J+ICOUNT)*NLF+1
FTEMP = ONE
L = 0
1055 K = L*LTEMP
GTEMP = ALPHAR*FTEMP
IF (INDIC(K)) GO TO 1070
C C CALCULATE MULTIPOLAR TERMS, EQU. (2.35).
Y(K) = TAU(K)/(FTEMP*R)
IF (ALPHAR.GT.RCP) GO TO 1070
MTEMP = (J+ICOUNT)*NMS+1
MLIM = NLPLUS-LPLUS
C C INITIALIZE SUMMATION QUANTITIES, EQU. (2.36).
ITEMP = LPLUS-L
JTEMP = L/LPLUS+1
FAC1 = FACT(ITEMP)
FAC2 = FACT(JTEMP)
E1 = TRUNCXITEMP,ALPHAR,X1)
E2 = TRUNCXJTEMP,ALPHAR,X2)
DTEMP = ZERO
HTEMP = GTEMP*FTEMP
C C SUM TERMS OF EQU. (2.37), RECURSION BY EQU. (2.38).
DO 1060 M=2,MLIM
ITEMP = ITEMP+1
JTEMP = JTEMP+1
1060 C C
D1 = DFLOAT(ITEMP)  SFFS 105
D2 = DFLOAT(JTEMP)  SFFS 106
FAC1 = FAC1*D1  SFFS 107
FAC2 = FAC2*D2  SFFS 108
N = M*TEMP  SFFS 109
DTEMP = DTEMP+SIGMA(N)*[(FAC1*E1-FAC2*E2)/NTEMP]  SFFS 110
X1 = X1+ALPHA/R  SFFS 111
X2 = X2+ALPHA/D2  SFFS 112
E1 = E1+X1  SFFS 113
E2 = E2+X2  SFFS 114

106C CONTINUE
C
C CALCULATE Y FROM EQ. (2.39).
Y(K) = Y(K)*TEMP*DEXPL(-ALPHA)*DTEMP/R  SFFS 115
1070 IF (L.EQ.LMAX2) GO TO 1075
  FTEMP = GTEMP  SFFS 116
  L = L+1  SFFS 117
  GO TO 1055  SFFS 118
1075 IF (JPLUS.EQ.IPLUS) GO TO 1080  SFFS 119
  J = JPLUS  SFFS 120
  GO TO 1050  SFFS 121
1080 IF (IPLUS.EQ.NLAG) GO TO 1095  SFFS 122
  J = IPLUS  SFFS 123
  GO TO 1045  SFFS 124
C
C CALCULATE \nu FUNCTIONS, EQ. (2.34).
1085 ICOUNT = 0  SFFS 125
  I = 0  SFFS 126
1090 ICOUNT = ICOUNT+1  SFFS 127
  IPLUS = I+1  SFFS 128
  IOF = I+NCHAN  SFFS 129
  N = (LABELR(IPLUS)-(LABELR(IPLUS)-1))/2  SFFS 130
  J = 0  SFFS 131
1095 JPLUS = J+1  SFFS 132
  JOF = J+NCHAN  SFFS 133
  ': = (LABELR(JPLUS)-1+M)*NL1  SFFS 134
  LTEMP = (.J+ICOUNT)*NL1  SFFS 135
  FTEMP = ZERN  SFFS 136
  L = 0  SFFS 137
1100 JTEMP = L+LTEMP  SFFS 138
  IF (FC(JTEMP).EQ.ZERO) GO TO 1105  SFFS 139
  ITEMP = L+N  SFFS 140
  FTEMP = FTEMP+FC(JTEMP)*YT(ITEMP)  SFFS 141
1105 IF (L.EQ.LMAX2) GO TO 1110  SFFS 142
  L = L+1  SFFS 143
  GO TO 1100  SFFS 144
1110 JTEMP = JPLUS+IOF  SFFS 145
  V(JTEMP) = FTEMP  SFFS 146
  IF (JPLUS.EQ.IPLUS) GO TO 1115  SFFS 147
  ITEMP = IPLUS+JOF  SFFS 148
  V(ITEMP) = FTEMP  SFFS 149
  J = JPLUS  SFFS 150
  GO TO 1095  SFFS 151
1115 IF (IPLUS.EQ.NCHAN) GO TO 1120  SFFS 152
  I = IPLUS  SFFS 153
  GO TO 1090  SFFS 154
C
C CALCULATE \phi FUNCTIONS FOR ZETA DESCRIPTORS.
1120 DO 1125 I=1,NCHAN  SFFS 155
  J = LABELR(I)  SFFS 156
  PHI(J) = FBESL(J)  SFFS 157
1125 CONTINUE  SFFS 158

1125 CONTINUE  SFFS 159
  IF (IECH(EQ,0)) GO TO 1135  SFFS 160
  DO 1130 I=1,NZG  SFFS 161
    IPLUS = NZETA(I)  SFFS 162
    J = LABELR(IPLUS)  SFFS 163
    K = I+NCHAN  SFFS 164
C
C THIS IS \phi FUNCTION IN EQ. (2.51).
1130 PHI(K) = GBESL(J)*HA(I)-FBESL(J)*HB(I)  SFFS 165
  IF (R.GT.RCK) GO TO 1130  SFFS 166
  IPLUS = NZETA(I)  SFFS 167
  K = LABELR(IPLUS)  SFFS 168
C  INTEGRATION OF HA AND HB, EQUATIONS (2.52) AND (2.53).
DTEMP = PI(X) * (R * ZETA(I)) * DR
HA(I) = HA(I) + FBESL(J) * DTEMP
HB(I) = HB(I) + GBESL(J) * DTEMP
1130 CONTINUE
C
1135 RETURN
END

SUBROUTINE INTSYS (F, W, A, B, Q, U, JCHAN, JPHI)
C
C  THIS ROUTINE INTEGRATES THE GIVEN COLUMN OF THE A, B, Q,
C  AND U INTEGRALS FROM R TO R + DR. JPHI AND JCHAN TELL WHICH
C  PHI TO ADD TO WHICH CHANNEL FOR THIS COLUMN.
C
C  DIMENSION
C   F(4), W(4), A(4), B(4), Q(18), U(18)
C
C  COMMON /BLK/
C   * NAUS, JPC, JPO, LL, LS, IPAR, JEXCH, NBSA(IS), LBSA(IS),
C   * LTES(4), JTES(4), LABEL(4), LABELB(4), INDIC(18),
C   * NZETA(18), NZETA10, LZETA10, LZETA10, NSTEP(2)
C
C  COMMON /DARK/
C   * WRES(4), BRRES(4), D(6), AC(6), SIGMA(18), TAU(18),
C   * FC(30), GC(50), P(3), FBESL(4), GBESL(4), Y(18), V(18),
C   * HA(18), HB(18), PHI(22), DELTA(2), RSAVE(20), RLIST(6),
C   * R, DR, RCX, RCP, ENERGY
C
C  COMMON /CNS/
C   * NCHAN, NLAG, NRES, NMAX, NMAX2, LMAX, LMAX2, MIG, MNG, MXG,
C   * NLF, NLG, NMS, NZG, NTOTAL, NFIES, NLISTS, MFILE, MLIST
C
C  COMMON /CONS/
C   * ZERO, ONE, TWO
C
C  LOGICAL INDIC
C
C  DOUBLE PRECISION
C   * WRES, BRRES, D, AC, SIGMA, TAU, FC, GC, P, FBESL, GBESL, Y, V,
C   * HA, HB, PHI, DELTA, RSAVE, RLIST, R, RCX, RCP, ZERO, ONE, TWO,
C   * F, W, A, B, Q, U, DR, ENERGY, DTEMP, FTEMP, GTEMP, HTMP,
C   * RM, RA1, RA2
C
C  C  CALCULATE F FUNCTIONS BY EQ. (1.15).
D 1025 I = 1, NCHAN
L = LABEL(I)
F(I) = GBESL(L) * A(I) - FBESL(L) * B(I)
1025 CONTINUE
C
F(JCHAN) = FI(JCHAN) + PHI(JPHI)
C
C  DIRECT POTENTIAL CALCULATION.
I = 0
1030 IPLUS = I + 1
IDF = I * NCHAN
DTEMP = ZERO
J = 0
1035 JPLUS = J + 1
JTEMP = JPLUS * IDF
C
NOTE THE USE OF V - TRANSPOSE IN THIS STATEMENT
DTEMP = DTEMP + V(JTEMP) * (JPLUS)
IF (JPLUS.EQ.0.NCHAN) GO TO 1040
J = JPLUS
GO TO 1035
1040 W(IPLUS) = DTEMP
IF (IPLUS.EQ.0.NCHAN) GO TO 1045
I = IPLUS
GO TO 1030
C
1045 IF (JEXCH.EQ.0) GO TO 1085  
IF (R.GT.RCX) GO TO 1085  
SINT 59  
SINT 60  
C  
C EXCHANGE POTENTIAL CALCULATION, INTEGRATION OF Q AND U  
C BY EQS. (1.16) AND (1.17).  
C  
RM = R**MNG  
M2G = 0  
I = 0  
IPLUS = I+1  
DTEMP = ZERO  
JTEMP = LABELR(IPLUS)  
FTEMP = DR*PIJTEMP)  
J = 0  
1050 CONTINUE  
IF (JPLUS.GT.1PLUS) GO TO 1060  
JDF = (I*(IPLUS+1)/2)*NLG*MNG  
GO TO 1065  
SINT 72  
1060 JDF = (I*(IPLUS+1)/2)*NLG*MNG  
1085 DTEMP = FTEMP*F(IPLUS)  
HTEMP = ZERO  
RM1 = RM  
RM2 = R*RM1  
DO 1075 L=MNG, MXG  
JTEMP = L+JDF  
IF (GCC(JTEMP),EQ.ZERO) GO TO 1070  
M2G = M2G+1  
HTEMP = HTEMP+GC(JTEMP)*U(M2G)*RM1-Q(M2G)/RM2  
U(M2G) = U(M2G)+GTEMP*RM1  
GO TO 1055  
SINT 73  
1070 CONTINUE  
RM1 = RM2  
RM2 = R*RM2  
SINT 74  
1075 CONTINUE  
JTEMP = LABELR(JPLUS)  
DTEMP = DTEMP+HTEMP*P(IJTEMP)  
IF (JPLUS.EQ.NCHAN) GO TO 1080  
J = JPLUS  
GO TO 1055  
SINT 75  
1080 W(IPLUS) = W(IPLUS)+DTEMP  
IF (IPLUS.EQ.NCHAN) GO TO 1085  
I = IPLUS  
GO TO 1090  
SINT 76  
C  
INTEGRATION OF A AND B BY EQS. (1.19) AND (1.20).  
1085 DO 1090 I=1,NCHAN  
DTEMP = DR*W(I)  
L = LABELR(I)  
A(I) = A(I)+DTEMP*FBESL(L)  
B(I) = B(I)+DTEMP*GBESL(L)  
GO TO 1095  
SINT 77  
1090 CONTINUE  
RETURN;  
END  
SUBROUTINE SAVINT  
C  
C THIS ROUTINE GENERATES FROM THE CURRENT VALUES OF THE  
C INTEGRALS THE REQUIRED MATRICES FOR CALCULATING THE R-MATRIX  
C AND CROSS SECTIONS.  
C  
DIMENSION NAME(2)  
DATA NAME / 6HSING ,6HTRIP /  
C  
COMMON /DBLK/  
* HNRN, IPC, JPC, LL, LS, JPAR, JEXCH, NBASES(13), LBASES(13),  
* LRES(4), JRES(4), LABELR(4), LABELB(4), INDIC(18),  
* NZETA(18), MZETA(18), LZETA(18), NSTEP(2)  
COMMON /VLBK/  
* WBES(4), RBES(4), D(6), AC(6), SIGMA(18), TAU(18),  
* FC(30), GC(30), PI(3), FBES(4), GBES(4), Y(18), V(18),  
* HA(18), HB(18), PHI(22), DELTA(2), RSAVE(20), RLIST(6),  
* H, DR, RCX, RCP, ENERGY  
SINT 78  
SINT 79  
SINT 80  
SINT 81  
SINT 82  
SINT 83  
SINT 84  
SINT 85  
SINT 86  
SINT 87  
SINT 88  
SINT 89  
SINT 90  
SINT 91  
SINT 92  
SINT 93  
SINT 94  
SINT 95  
SINT 96  
SINT 97  
SINT 98  
SINT 99  
SINT 100  
SINT 101  
SINT 102  
SINT 103  
SINT 104  
SINT 105  
SINT 106  
SINT 107  
SINT 108  
SINT 109  
SINT 110  
SSAV 0  
SSAV 1  
SSAV 2  
SSAV 3  
SSAV 4  
SSAV 5  
SSAV 6  
SSAV 7  
SSAV 8  
SSAV 9  
SSAV 10  
SSAV 11  
SSAV 12  
SSAV 13  
SSAV 14  
SSAV 15  
SSAV 16  
SSAV 17
COMMON /CNTS/
* NCHAN, NLG, NBES, NMAX, NMAXZ, LMAX, LMAXZ, MMG, MNG, MGX,
* NLF, NLS, NGS, NTOTAL, NFILES, NLISTS, NFILE, MLIST
COMMON /INTL/
* F(4,22), W(4,22), A(4,22), U(4,22), O(18,22), U(18,22)
COMMON /CONS/
* ZERO, ONE, TWO
COMMON /BORN/
* T(8,8), V(4,4,2), T(4,4), L(4,4)
C
LOGICAL INDIC, LB
C
DOUBLE PRECISION
* WRES, RHES, D, AC, SIGMA, TAU, FC, GC, P, FBESL, GBESL, Y, V,
* H, H, PHI, DELTA, RSAVE, RLIST, R, DR, RCX, RCY, ENERGY,
* F, W, A, B, Q, Q, ZERO, ONE, TWO, T, V, TC, TB, DTEMP,
* DTEMP, ATEMP(4,22), BTEMP(4,22), EXCH(18,22), (X12,22)
C
100 FORMAT (1H1)
101 FORMAT (12H INTEGRATION INTERRUPTED AT R = sF7.3,1H+,s5X,
* 12H ELAPSED TIME, F9.3,9H SECONDS.)
102 FORMAT (3H PARTIAL WAVE SPECIFICATION...16X,4HE = sF7.4,
* 6H, L = 12,3H, sA4, NL2ET,s)
C
CALL GETIME (TEMP)
TEMP = TEMP/60.
WRITE (16,100)
WRITE (6,101) R, TEMP
WRITE (6,102) ENERGY, LL, NAME(LS+1)
KEY = 0
C
C CALCULATE AND STORE THE EXCHANGE MATRIX ELEMENTS.
IF (JEXCH.EQ.0) GO TO 1020
DO 1015 K=1,NTOTAL
1015 I = NZETA(K)
J = NZET(A)
ITEMP = LABELR(I)
JTEMP = LABELR(J)
IF (J,G.T,.1) GO TO 1005
JPLUS = J+1*(J-1)/2
L = JTEMP*(ITEMP*TTEMP-1)/2
GO TO 1010
1005 JPLUS = J+1*(J-1)/2
L = JTEMP*(ITEMP+JTEMP-1)/2
1010 JPLUS = (JPLUS-1)*NLG-MMG
DTEMP = ZERO
IF (LZET(A),E.Q.0) DTEMP = AC(LI, I)
I = LMZET(A)+JPLUS
EXCH(K,M) = GC(I)*DTEMP*(Q(K,M)-U(K,M))
1015 CONTINUE
C
C STORE THE A AND B INTEGRALS.
1020 DO 1025 J=1,NTOTAL
1025 I = 1,NCHAN
ATEMP(I,J) = A(I,J)
BTEMP(I,J) = B(I,J)
1025 CONTINUE
C
DO 1030 J=1,NCHAN
ATEMP(I,J) = BTEMP(J,1-J)-ONE
1030 CONTINUE
C
IF (JEXCH.EQ.0) GO TO 1040
DO 1035 K=1,NGZ
I = NZETA(K)
J = K+MCHAN
ATEMP(I,J) = ATEMP(I,J)+HA(K)
BTTEMP(I,J) = BTEMP(I,J)+HB(K)
1035 CONTINUE
C
LOAD THE X MATRIX FOR CROSS-SECTION CALCULATION.
1040 DO 1045 J=1,NTOTAL
1045 I = 1,NCHAN
X(I,J) = BTEMP(I,J)
1045 CONTINUE
   IF (JEXCH.EQ.0) GO TO 1055
   DO 1050 K=1,NZG
   I = K*NCHAN
   X(I,J) = EXCH(K,J)
1050 CONTINUE
   IF (J+G*T*NCHAN) X(J,J) = X(J,J)-ONE
1055 CONTINUE
   CALL OUTPUT (X,ATEMP)
   CALL PROJECTION CONTROL SET TO 1 WILL SKIP PROJECTION
   IF (JPC.EQ.1) RETURN
   THIS SECTION PROJECTS THE CONTENTS OF ATEMP AND BTEMP TO
   INFINITY.
   200 FORMAT (5X,9D14.6)
   201 FORMAT (3H///21H INTEGRAL PROJECTION///)
   202 FORMAT (///5H COLS,13)
   KEY ONLY LETS CONTROL PASS THIS POINT ONCE.
   IF (KEY.EQ.1) RETURN
   WRITE (5,201)
   GET TRANSFORMATION MATRIX.
   CALL TFMN
   LOOP THRU INTEGRAL SETS FOR EACH ZETA.
   NCHAN2 = 2*NCHAN
   WRITE (6,201)
   DO 1070 K=1,NTUTAL
   WRITE (6,202) K
   DO 1060 I=1,NCHAN
   J = I*NCHAN
   CTEMP(I) = ATEMP(I,K)
   CTEMP(J) = BTEMP(I,K)
1060 CONTINUE
   WRITE (6,200) (CTEMP(I),I=1,NCHAN2)
   DO 1065 I=1,NCHAN
   ATEMP(I,K) = ZERO
   BTEMP(I,K) = ZERO
   J = I*NCHAN
   DO 1065 M=1,NCHAN2
   ATEMP(I,K) = ATEMP(I,K)+T(I,M)*CTEMP(M)
   BTEMP(I,K) = BTEMP(I,K)+T(I,M)*CTEMP(M)
1065 CONTINUE
   WRITE (6,200) (ATEMP(I,K),I=1,NCHAN), (BTEMP(I,K),I=1,NCHAN)
1070 CONTINUE
   WRITE (6,100)
   KEY = 1
   GO TO 1040
   END

SUBROUTINE OUTPUT (X,E)
   CALL OUTPPUT (X,E)
   THIS ROUTINE TAKES THE MATRICES CONSTRUCTED FROM THE CURRENT
   VALUES OF THE INTEGRALS AND CALCULATES THE R-MATRIX,
   T-MATRIX, AND PARTIAL WAVE CROSS SECTIONS.
   DIMENSION X(22,22), E(4,22), R(4,4), S(4,4), T(4,4),
   VECT(22), IN(22), JCN(22), NORD(22)
   COMMON /IBLK/
   * NRUN, IPC, JPC, LL, LS, IPAR, JEXCH, NBASIS(3), LBASIS(3),
   * LBES(4), JBES(4), LABELR(4), LABELR(4), INDIC(18),
   * NZETA(18), NZETA(18), LZETA(18), NSTEP(2)

SOUT -0
SOUT 1
SOUT 2
SOUT 3
SOUT 4
SOUT 5
SOUT 6
SOUT 7
SOUT 8
SOUT 9
SOUT 10
SOUT 11
SOUT 12
COMMON /DBLK/
   * WBES(4), RBES(4), D(6), AC(6), SIGMA(18), TAU(10),
   * PC(30), GCL(50), P(3), FBESL(4), GBESL(4), Y(18), V(16),
   * HA(18), HBI(18), PHI(22), DELTA(2), RSAVE(20), RLIST(6),
   * Z, DZ, RCM, RCP, ENERGY
COMMON /CNVS/
   * NCHAN, NLAE, NBES, NMAX, NMAX2, LMAX, LMAX2, MNG, MNG, MXG,
   * NLF, NLG, NMS, NZG, NTOTAL, NFIES, NLISTS, MFIES, MLIST
COMMON /IN/A/
   * F(4,22), W(4,22), A(4,22), B(4,22), Q(18,22), U(18,22)
COMMON /CONS/
   * ZERO, ONE, TWO
C
LOGICAL INDIC
C
DOUBLE PRECISION
   * WBES, RBES, D, AC, SIGMA, TAU, FC, GC, P, FBESL, GBESL, Y, V,
   * HA, HB, PHI, DELTA, RSAVE, RLIST, Z, DZ, ENERGY, RCM, RCP,
   * F, W, A, B, Q, U, ZERD, ONE, TWO, X, E, R, S, T,
C
   * FACT, DEGN, DTMP, VECT, EPS, DFLAT
C
   * NOTE THAT F IS ONLY IN USE DURING EXECUTION OF INTSYS.
   * EQUIVALENCE
   * (VECT(1), F(1)), (IR(1), F(23)),
   * (NORD(1), F(67)), (JC(1), F(45))
C
   DATA EPS / 1.00D-10 /
C
100 FORMAT (/5X,4D19.9)
101 FORMAT (/3H R MATRIX///)
102 FORMAT (/3H REAL PART OF T MATRIX///)
103 FORMAT (/3H IMAG PART OF T MATRIX///)
104 FORMAT (/3H PARTIAL WAVE CROSS-SECTIONS///)
105 FORMAT (/3H PHASE SHIFT = ,D16.9,5H RAD///)
106 FORMAT (/3H ABORT///)
C
   * R-MATRIX CALCULATION.
   * WRITE (6,101)
   * I = 1
   * CALL SIMUL (22,22,X,NTOTAL,NTOTAL,VECT,IR,JC,NORD,EPS,DTMP)
   * IF (DTMP.EQ.ZERO) GO TO 1095
C
1005 DO 1020 I=1,NCHAN
1010 J=1,NCHAN
   DTEMP = ZERO
   DU 1010 K=1,NTOTAL
   DTEMP = DTEMP+D(I,K)*X(K,J)
1010 CONTINUE
R(I,J) = DTEMP
1015 CONTINUE
   WRITE ((6,100) (R(I,J), J=1,NCHAN)
1020 CONTINUE
C
   * IF CALCULATION IS SINGLE CHANNEL, CALCULATE PHASE SHIFT.
   * IF (NCHAN,GT,1) GO TO 1025
   DTEMP = DATAN(R(I,1))
   WRITE ((6,105) DTEMP
C
   * T-MATRIX CALCULATION.
1025 DO 1035 I=1,NCHAN
1030 J=1,NCHAN
   DTEMP = ZERO
   DU 1030 K=1,NCHAN
   DTEMP = DTEMP+R(I,K)*R(K,J)
1030 CONTINUE
   IF (I.EQ.0) DTEMP = DTEMP+ONE
S(I,J) = DTEMP
1035 CONTINUE
C
   * I = 2
   CALL SIMUL (4,4,S,NCHAN,NCHAN,VECT,IR,JC,NORD,EPS,DTMP)
   IF (DTMP.EQ.ZERO) GO TO 1095
C
1040 WRITE ((6,102)
DO 1055 I=1,NCHAN
DO 1050 J=1,NCHAN
DTEMP = ZERO
DO 1045 K=1,NCHAN
DTEMP = DTEMP*R(I,K)*S(K,J)
1045 CONTINUE
T(I,J) = -TWO*DTEMP
1050 CONTINUE
WRITE (6,100) (T(I,J), J=1,NCHAN)
1055 CONTINUE
WRITE (6,103)
DO 1070 I=1,NCHAN
DO 1065 J=1,NCHAN
DTEMP = ZERO
DO 1060 K=1,NCHAN
DTEMP = DTEMP*T(I,K)*R(K,J)
1060 CONTINUE
S(I,J) = DTEMP
1065 CONTINUE
WRITE (6,100) (S(I,J), J=1,NCHAN)
1070 CONTINUE
C CROSS SECTION CALCULATION.
DEGEN = DFLOAT((2*L+1)*(2*L+1))/4.000
WRITE (6,104)
DO 1090 I=1,NLAG
FA = ONE/DFLOAT(2*LBASIS(I)*LBASIS(I))
ENERGY = ONE/DFLOAT(NR*BASIS(I)**2))
DO 1085 J=1,NLAG
DTEMP = ZERO
DO 1080 K=1,NCHAN
IF (LABELR(K),NE.J) GO TO 1080
DO 1075 L=1,NCHAN
IF (LABELR(L),NE.J) GO TO 1075
DTEMP = DTEMP*T(K,L)**2+S(K,L)**2
1075 CONTINUE
1080 CONTINUE
R(I,J) = DTEMP*FA*DEGEN
1085 CONTINUE
WRITE (6,100) (R(I,J), J=1,NLAG)
1090 CONTINUE
RETURN
C 1095 WRITE (6,106) I
RETURN
END

SUBROUTINE SIMUL (NR,NC,A,N,NP,TEMP,IR,JC,NORD, EPS, DET)
C THIS ROUTINE PERFORMS IN SITU INVERSION OF THE N BY N
C MATRIX A, IT REQUIRES FOUR AUXILIARY VECTORS - TEMP, IR, JC,
C AND NORD. THE SMALLEST ALLOWABLE PIVOT IS SPECIFIED BY EPS.
C THE DETERMINANT OF A IS RETURNED IN DET. IF A IS SINGULAR,
C DET IS SET TO ZERO. IF A IS PART OF A SYSTEM AX=B, THE B
C VECTORS MAY BE PLACED IN COLUMNS N+1 THROUGH NP OF A AND THE
C CORRESPONDING X WILL BE RETURNED IN THOSE COLUMNS.
C THE ACTUAL SIZE OF THE MATRIX BEING USED IN NR BY NC. THE
C EFFECTIVE SIZE OF THE PROBLEM IS N BY NP.
C DIMENSION A(NR,NC), TEMP(N), IR(N), JC(N), NORD(N)
C DOUBLE PRECISION A, TEMP, EPS, DET, ZRO, ONE, D
C DATA ZRO, UNE/ 0.00, 1.00 /
C IF (N.GT.0) GO TO 1010
1005 DET = ZRO
RETURN
C
1010 DET = ONE
IR(I) = 0
JC(J) = 0

C
DO 1060 K=1,N
C
C  FIND MAXIMUM PIVOT.
N = ZRO
KLES = K-1
DO 1030 I=1,N
DO 1015 L=1,KLES
IF (I.EQ.IRL(L)) GO TO 1030
1015 CONTINUE
DO 1025 J=1,N
DO 1020 M=1,KLES
IF (J.EQ.JCM(M)) GO TO 1025
1020 CONTINUE
IF (DBAS(D).GT.DABS(A(I,J))) GO TO 1025
D = A(I,J)
IR(K) = I
JC(K) = J
1025 CONTINUE
IF (DBAS(D).LT.EPS) GO TO 1005
DET = DET*D
L = IR(K)
M = JC(K)

C
C  NORMALIZE ROW L.
DO 1040 J=1,NP
IF (J.EQ.M) GO TO 1035
A(L,J) = A(L,J)/D
GO TO 1040
1035 A(L,M) = INC/D
1040 CONTINUE
C
C  CLEAR COLUMN M IN EACH ROW.
DO 1055 K=1,N
IF (I.EQ.L) GO TO 1055
D = A(I,M)
DO 1050 J=1,NP
IF (J.EQ.M) GO TO 1045
A(I,J) = A(I,J) - D*AML(J)
GO TO 1050
1045 A(I,J) = -D*AML(M)
1050 CONTINUE
1055 CONTINUE
C
C  REORDERING OF INVERSE.
DO 1065 K=1,N
J = JC(K)
NORD(I) = J
1065 CONTINUE
C
C  COUNT THE NUMBER OF EXCHANGES REQUIRED TO REORDER NORD.
I = 0
M = N
1070 J = 1
DO 1075 K=2,M
IF (NORD(K).GT.NORD(K-1)) GO TO 1075
L = NORD(K-1)
NORD(K-1) = NORD(K)
NORD(K) = L
I = I+1
1075 CONTINUE
IF (J.EQ.1) GO TO 1080
M = J
GO TO 1070
1080 IF (2*(I/2).EQ.1) GO TO 1085
DET = -DET
SSIM 22
SSIM 23
SSIM 24
SSIM 25
SSIM 26
SSIM 27
SSIM 28
SSIM 29
SSIM 30
SSIM 31
SSIM 32
SSIM 33
SSIM 34
SSIM 35
SSIM 36
SSIM 37
SSIM 38
SSIM 39
SSIM 40
SSIM 41
SSIM 42
SSIM 43
SSIM 44
SSIM 45
SSIM 46
SSIM 47
SSIM 48
SSIM 49
SSIM 50
SSIM 51
SSIM 52
SSIM 53
SSIM 54
SSIM 55
SSIM 56
SSIM 57
SSIM 58
SSIM 59
SSIM 60
SSIM 61
SSIM 62
SSIM 63
SSIM 64
SSIM 65
SSIM 66
SSIM 67
SSIM 68
SSIM 69
SSIM 70
SSIM 71
SSIM 72
SSIM 73
SSIM 74
SSIM 75
SSIM 76
SSIM 77
SSIM 78
SSIM 79
SSIM 80
SSIM 81
SSIM 82
SSIM 83
SSIM 84
SSIM 85
SSIM 86
SSIM 87
SSIM 88
SSIM 89
SSIM 90
SSIM 91
SSIM 92
SSIM 93
SSIM 94
SSIM 95
SSIM 96
C

ROW AND COLUMN INTERCHANGES.

1085 DO 1100 J=1,NP
DO 1090 I=1,N
L = JCI(I)
M = IR(I)
TEMP(L) = A(M,J)
1090 CONTINUE
DO 1095 I=1,N
A(I,J) = TEMP(I)
1095 CONTINUE
1100 CONTINUE
DO 1110 J=1,N
DO 1115 I=1,N
L = JCI(J)
M = IR(J)
TEMP(M) = AT(I,L)
1110 CONTINUE
DO 1115 J=1,N
A(I,J) = TEMP(J)
1115 CONTINUE
RETURN
END

SUBROUTINE TFMN

THIS ROUTINE CONSTRUCTS THE APPROXIMATE MATRICANT.

COMMON /IBLK/
* MRU, XPC, JPC, LL, LS, IPAR, IEXCH, NBASIS(3), LBASIS(3),
* LBS(4), RBS(4), LABELR(4), LABELL(4), INDIC(18),
* NZETA(18), NZETA(18), LZETA(18), NZETA(2),
* COMMON /DBLK/
* WBES(4), RRES(4), D(6), A(6), SIGMA(18), TAU(18),
* FC(30), GC(30), P(3), PBE(4), GBSL(4), Y(18), V(18),
* HA(18), H(18), PHI(22), DELTA(2), RCSAVE(20), RLIST(18),
* R, DR, RCX, RCP, ENERGY,
COMMON /CINT/
* NCHAN, NLAG, NR, NMAX, NMAX2, LMAX, LMAX2, MMG, MG, MG,
* NL, NLG, RMS, NZG, NTOA, NFILES, NLISTS, MFILE, MLIST,
COMMON /CONS/
* ZERO, ONE, TWO
COMMON /RORN/
* T(8,8), VC(4,4,2), TB(4,4), LB(4,4)

LOGICAL INDIC, LB

DOUBLE PRECISION
* WBES, RRES, D, A, SIGMA, TAU, FC, GC, P, PBE(4), GBSL(4), Y, V,
* HA, HB, PHI, DELTA, RCSAVE, RLIST, R, DR, RCX, RCP, ENERGY,
* ZERO, ONE, TWO, T, VC, TB, TEMP, E, F, G, H, W, U, X,
* CM(20), CP(20), SM(20), SP(20)

101 FORMAT (///23H TRANSFORMATION MATRIX,///)
102 FORMAT (5X,10D15.6)

C

ZEROTH ORDER MATRIX.

NCHAN2 = 2*NCHAN
DO 1001 G=1,NCHAN2
DO 1005 J=1,N
T(I,J) = ZERO
1005 CONTINUE
T(J,I) = ZERO
1010 CONTINUE

C

GET BESSEL FUNCTION COEFFICIENTS IN TB AND POTENTIAL
C

COEFFICIENTS IN VC.

CALL CONST
FIRST ORDER TERMS.

L = 2*(LL+LMAX2)
DO 1040 I=1,NCHAN
IPLUS = I+NCHAN
LI = LABELB(I)
DO 1040 J=1,NCHAN
JPLUS = J+NCHAN
LJ = LABELB(J)
W = WBES(I)-WBES(J)
CALL TRIG (CM,SM,L,W,R)
W = WBES(I)+WBES(J)
CALL TRIG (CP,SP,L,W,R)

DO INNER SUMS.
LIM1 = LBES(LI)+1
LIM2 = LBES(LJ)+1
M13 = 1,LMAX2
IF (VC(I,J,M13),EQ,ZERO) GO TO 1040
DO 1035 M12=1,LIM1
M1 = 1,LIM1
MSUM = M1*X+M12*MSUM
E = (CM*MSUM)-CP(MSUM)
F = SM(MSUM)+SP(MSUM)
G = SM(MSUM)+SP(MSUM)
H = CM(MSUM)+CP(MSUM)
TEMP = TB(I,M11)*TB(J,M12)*VC(I,J,M13)

IF (LB(LI,M11)) GO TO 1020
IF (LB(LJ,M12)) GO TO 1015

FIRST FALSE, SECOND FALSE, PRODUCT IS S*S.
W = TEMP*S
U = TEMP*H
X = TEMP*E
GO TO 1030

FIRST FALSE, SECOND TRUE, PRODUCT IS S*R.
W = TEMP/H
U = TEMP*S
X = TEMP/E
GO TO 1030

IF (LB(LJ,M12)) GO TO 1025

FIRST TRUE, SECOND FALSE, PRODUCT IS R*S.
W = TEMP*E
U = TEMP*F
X = TEMP*G
GO TO 1030

FIRST TRUE, SECOND TRUE, PRODUCT IS R*R.
W = TEMP*F
U = TEMP*E
X = TEMP*H

ACCUMULATE SUMS IN MATRIX ELEMENTS.
1030 T(I,J) = T(I,J)+W
T(I,JPLUS) = T(I,JPLUS)+U
T(JPLUS,J) = T(JPLUS,J)+X
T(JPLUS,JPLUS) = T(JPLUS,JPLUS)+W
1035 CONTINUE
1040 CONTINUE

WRITE (6,102) (T(I,J),J=1,NCHAN)
1045 CONTINUE
RETURN
FND
SUBROUTINE CONST

C THIS ROUTINE CREATES ARRAYS OF BESSEL FUNCTION COEFFICIENTS
C AND THE MULTIPOLe COEFFICIENTS.
C
COMMON /IBLK/
C * NRUN, IPC, JPC, LL, LS, IPAR, JEXCH, NBASE(3), LBASIS(3),
C * LBE(4), JBE(4), LABELR(4), LABELL(4), INDIC(18),
C * NETA(18), MZETA(18), LVZETA(18), NVSTEP(2)
C SCON 0
C SCON 1
C SCON 2
C SCON 3
C SCON 4
C SCON 5
C SCON 6
C SCON 7
C SCON 8
C SCON 9
C SCON 10
C SCON 11
C SCON 12
C SCON 13
C SCON 14
C SCON 15
C SCON 16
C SCON 17
C SCON 18
C SCON 19
C SCON 20
C SCON 21
C SCON 22
C SCON 23
C SCON 24
C SCON 25
C SCON 26
C SCON 27
C SCON 28
C SCON 29
C SCON 30
C SCON 31
C SCON 32
C SCON 33
C SCON 34
C SCON 35
C SCON 36
C SCON 37
C SCON 38
C SCON 39
C SCON 40
C SCON 41
C SCON 42
C SCON 43
C SCON 44
C SCON 45
C SCON 46
C SCON 47
C SCON 48
C SCON 49
C SCON 50
C SCON 51
C SCON 52
C SCON 53
C SCON 54
C SCON 55
C SCON 56
C SCON 57
C SCON 58
C SCON 59
C SCON 60
C SCON 61
C SCON 62
C SCON 63
C SCON 64
C SCON 65
C SCON 66
C SCON 67
C SCON 68
C SCON 69
C SCON 70

LOGICAL INDIC, LB

DOUBLE PRECISION

101 FORMAT (12H POTENTIAL CONSTANTS, 12X, 4115)
102 FORMAT (2H 12.1H, 12.1H, 4015.6)

CALCULATION OF BESSEL COEFFICIENTS. LOGICAL ARRAY LB KEYS
A COEFFICIENT IN TR AS S WITH .FALSE. AND R WITH .TRUE.

DO 1030 I=1,NBES
L = LBE(S)
W = WBES(I)
X = DSORT(W)
LPLUS = L+1
DO 1025 J=1,LPLUS
M = J-1
TEMP = FACT(L+M)/(FACT(W)*FACT(M)*FACT(L-M)*X)
M = L-M
K = MOD(M,4)+1

GO TO (1005,1010,1015,1020), K
1005 TBI(J) = TEMP
LB(L,J) = .TRUE.
GO TO 1025
1010 TBI(J) = .FALSE.
LB(L,J) = .FALSE.
GO TO 1025
1015 TBI(J) = TEMP
LB(L,J) = .TRUE.
GO TO 1025
1020 TBI(J) = TEMP
LB(L,J) = .FALSE.
GO TO 1025

CALCULATION OF MULTIPOLe COEFFICIENTS.

1035 I = 0
1040 I = I + 1
IPLUS = I+1
NI = LABELR(IPLUS)
M = (NI*(NI-1))/2
J = NBASIS(NI)
JPLUS = J+1
NJ = LABEL(JPLUS)
N = (NJ-1*M)+NLF+1
NJ = NBASIS(NJ)
LTEMP = (J+ICOUNT)*NLF+1
L = 1
1050 JTEMP = L*LTEMP
ITEMP = L+N
VC(JPLUS,JPLUS,L) =
* FC(JTEMP)*TAU(ITEMP)*(DFLOAT(NI+NZ)/DFLOAT(NI+NZ))*L
VC(JPLUS,JPLUS,L) = VC(JPLUS,JPLUS,L)
IF (L.EQ.LMAX2) GO TO 1055
L = L+1
GO TO 1050
1055 IF (JPLUS.EQ.IPLUS) GO TO 1060
J = JPLUS
GO TO 1045
1060 IF (IPLUS.EQ.NCHAN) GO TO 1065
I = IPLUS
GO TO 1040
C
C LIST THE VC ARRAY.
1065 WRITE (6,101) (M,N=1,LMAX2)
DO 1070 I=1,NCHAN
DO 1070 J=1,I
WRITE (6,102) I, J, (VC(I,J,M),M=1,LMAX2)
1076 CONTINUE
RETURN
END

SUBROUTINE TRIG (C,S,L,K,R)
C
C THIS ROUTINE RECURSIVELY GENERATES STRINGS OF THE SINE AND
C COSINE INTEGRALS USED FOR EVALUATING THE MATRICANT.
C
DIMENSION C(L), S(L)
C
COMMON /CONS/
* ZER, ONE, TWO
C
DOUBLE PRECISION
* C, S, K, R, TEMP, FAC, X, DS, DC, FTEMP, GTEMP, SL, CL,
* ZER, ONE, TWO, EPS, DFLOAT
C
DATA FPS / 1.0D-26 /
C
DO 1000 I=1,L
S(I) = ZERO
C(I) = ZERO
1000 CONTINUE
TEMP = ONE/R
FAC = TEMP
IF (X.EQ.ZERO) GO TO 1020
I = 1
1005 I = I+1
FAC = FAC*TEMP
IF (FAC*EPS) GO TO 1005
X = K*R
DS = DSIN(X)/X
DC = DCOS(X)/X
FTEMP = FAC*DC
GTEMP = -FAC*DS
1010 FAC = R*FAC
SL = FAC*DC-DFLOAT(I)*GTEMP/K
CL = FAC*DS+DFLOAT(I)*FTEMP/K
GTEMP = CL
FTEMP = SL
I = I-1
IF (I.GT.L) GO TO 1010
S(I) = SL
C(I) = CL
IPLUS = 1
I = I+1
1015 FC = RC*FC
c(1) = FC/DC-DFLOAT(IPLUS)*G(IPLUS)/K
IPLUS = 1
IF (I.GT.0) GO TO 1015
RETURN
1020 I = 1
1025 FC(i) = FC/DFLOAT(I)
IF (I.EQ.0) RETURN
FC = FC*TEMP
I = I+1
GO TO 1025
END

SUBROUTINE GREENS (F,G,L,W, Z)

C THIS ROUTINE CALCULATES RICATTI-BESSLE AND NEUMANN FUNCTIONS
FROM Eqs. (2.11) AND (2.2).
C
COMMON /CONS/ ZERO, ONE, TWO
DOUBLE PRECISION ZERO, ONE, TWO
DOUBLE PRECISION DFLOAT

C COMPUTE THE TWO SUMS.
S1 = ZERO
S2 = ZERO
WZ = W*Z
ZZ = TWO*WZ
SIGN = ONE
X = ONE
M = 0
10 S1 = S1+SIGN*X
LM = L-M
IF (LM.EQ.0) GO TO 20
M = M-1
X = X+DFLOAT((L+M)*LM)/(IZZ*DFLOAT(M))
S2 = S2+SIGN*X
LM = L-M
IF (LM.EQ.0) GO TO 20
M = M-1
X = X+DFLOAT((L+M)*LM)/(IZZ*DFLOAT(M))
SIGN = -SIGN
GO TO 10
C
C ASSIGN SUMS TO REAL AND IMAGINARY PARTS.
20 K = 1+MOD(L,4)
GO TO (30,40,50,60), K
C
30 R = S1
S = S2
GO TO 70
40 R = S2
S = S1
GO TO 70
50 R = -S1
S = -S2
GO TO 70
60 R = -S2
S = S1
C
C EVALUATE FUNCTIONS FROM Eqs. (2.2A) AND (2.2B).
70 S1 = DCSIN(WZ)
S2 = DCOS(WZ)
WZ = DSRQH(W)
F = (R*S1+S*S2)/WZ
G = (S*S1-R*S2)/WZ
RETURN
END
DOUBLE PRECISION FUNCTION TRUNCX (J, R, X) 

C THIS ROUTINE EVALUATES THE TRUNCATED EXPONENTIAL 
C FROM EQ. (2.25). 
C
COMMON /CONS/ ZERO, ONE, TWO 
DOUBLE PRECISION ZERO, ONE, TWO 
DOUBLE PRECISION SUM, R, X, DFLOAT 
C
I = 0 
X = ONE 
SUM = ZERO 
1010 SUM = SUM + X 
IF (I.EQ.J) GO TO 1020 
I = I+1 
X = X*R/DFLOAT(I) 
GO TO 1010 
1020 TRUNCX = SUM 
RETURN 
END

DOUBLE PRECISION FUNCTION FACT (M) 

C THIS ROUTINE CALCULATES M FACTORIAL. M GREATER THAN 14 RESULTS 
C IN INTEGER OVERFLOW IF INTEGER ARITHMETIC IS USED. 
C
COMMON /CONS/ ZERO, ONE, TWO 
DOUBLE PRECISION ZERO, ONE, TWO 
DOUBLE PRECISION DTEMP, DFLOAT 
C
IF (M.GT.1) GO TO 5 
FACT = ONE 
RETURN 
5 IF (M.GT.14) GO TO 15 
I = 1 
DO 10 J=2, M 
I = I+1 
10 CONTINUE 
FACT = DFLOAT(I) 
RETURN 
15 DTEMP = ONE 
DO 20 J=2, M 
DTEMP = DTEMP*DFLOAT(J) 
20 CONTINUE 
FACT = DTEMP 
RETURN 
END

DOUBLE PRECISION FUNCTION PLJ (K, L1, L2, L3, L4, J) 

C THIS ROUTINE CALCULATES THE INTEGRAL OF THE LEGENDRE 
C POLYNOMIAL IN THE COUPLED ANGULAR BASIS FROM EQ. (2.42). 
C
DOUBLE PRECISION DFLOAT, C6J, SPC3J, FTEMP 
C
FTEMP = DFLOAT((2*L1+1)*(2*L2+1)*(2*L3+1)*(2*L4+1)) 
FTEMP = DSQRT(FTEMP)/DFLOAT((-1)**((L2+L4+J))) 
PLJ = FTEMP*C6J*(L1*L1+L3*L4+1)*SPC3J*(L1+L3)*SPC3J*(L2+L4) 
RETURN 
END
DOUBLE PRECISION FUNCTION C6J (J1, J2, J3, L1, L2, L3)

THIS ROUTINE CALCULATES THE 6-J COEFFICIENT FROM Eqs. (2.43), (2.45), AND (2.46).

COMMON /CONS/ ZERO, ONE, TWO
DOUBLE PRECISION ZERO, ONE, TWO
DOUBLE PRECISION DTEMP, FTEMP, GTEMP, FACT, DFLOAT, DELT

DTEMP = DELT(J1, J2, J3) * DELT(J1, L2, L3) * DELT(J1, J2, L3) *
       DELT(L1, L2, J3)

IF (DTEMP.EQ.ZERO) RETURN

11 = J1 + J2 + J3
12 = J1 + L2 + L3
13 = J1 + J2 + L3
14 = L1 + L2 + J3
15 = J1 + J2 + L1 + L2
16 = J2 + J3 + L2 + L3
17 = J3 + J1 + L3 + L1
KMIN = I1
IF (I1.GT.KMIN) KMIN = I1
IF (I2.GT.KMIN) KMIN = I2
IF (I3.GT.KMIN) KMIN = I3
IF (I4.GT.KMIN) KMIN = I4
KMAX = I5
IF (KMAX.GT.16) KMAX = 16
IF (KMAX.GT.17) KMAX = 17
FTEMP = ZERO

GTEMP = FACT(KMIN+1)*DFLOAT(-1)**KMIN

DO 5 K = KMIN, KMAX
   FTEMP = FTEMP*GTEMP/(FACT(K-11)*FACT(K-12)*FACT(K-13)*
                FACT(K-14)*FACT(15-K)*FACT(16-K)*FACT(17-K))
   GTEMP = -GTEMP*DFLOAT(K+2)
5 CONTINUE

C6J = DTEMP*FTEMP
RETURN
END

DOUBLE PRECISION FUNCTION SPC3J (J1, J2, J3)

THIS ROUTINE CALCULATES THE SPECIAL FORM OF THE 3-J COEFFICIENT FROM Eq. (2.47).

COMMON /CONS/ ZERO, ONE, TWO
DOUBLE PRECISION ZERO, ONE, TWO
DOUBLE PRECISION FACT, DFLOAT, DELT

SPC3J = ZERO
JJ = J1 + J2 + J3
J = JJ/2
IF (2*J.NE.JJ) RETURN

SPC3J = DFLOAT(-1)**J * DELT(J1, J2, J3) * FACT(J) /
        (FACT(J-J1)*FACT(J-J2)*FACT(J-J3))
RETURN
END

DOUBLE PRECISION FUNCTION DELT (I, J, K)

THIS ROUTINE CALCULATES THE TRIANGLE RULE COEFFICIENT FROM Eq. (2.44).

COMMON /CONS/ ZERO, ONE, TWO
DOUBLE PRECISION ZERO, ONE, TWO
DOUBLE PRECISION FACT

...
C
DELT = ZERO
L = I+J-K
IF (L.LT.0) RETURN
M = I-J+K
IF (M.LT.0) RETURN
N = I+J+K
IF (N.LT.0) RETURN
DELT = D*SQR(FACT(I)*FACT(J)*FACT(N)/FACT(I+J+K))
RETURN
END

DOUBLE PRECISION FUNCTION DFLOAT (I)
C
THIS ROUTINE PROVIDES A DOUBLE PRECISION FLOAT FUNCTION.
C
DFLOAT = DALLF(REAL(I))
RETURN
END

SUBROUTINE LIST
C
THIS ROUTINE CAN BE USED TO LIST ALL INTERNAL ARRAYS.
C
DIMENSION WORD(8)
DATA WORD / 6H D, 6H SIGMA, 6H AC, 6H FC, *
       6H GC, 6H INDIC, 6H TAU, 6H ZETA /
C
DIMENSION INDEX(10)
DATA INDEX / 0,1,2,3,4,5,6,7,8,9 /
C
COMMON /IRLK/
   * NRUN, IPC, JPC, LL, LS, IPAR, JEXCH, NBASIS(3), LBASIS(3),
   * LBES(4), JBEA(4), LABELR(4), LABEL(4), INDIC(18),
   * NZETA(18), NZETA(18), LZETA(18), NSTEP(2)
COMMON /IDLK/
   * WBE5(4), RBES(4), D(6), AC(6), SIGMA(18), TAU(18),
   * FC(20), GC(50), P(3), FBE5(4), GBE5(4), Y(18), Y(18),
   * HA(18), HB(18), PHI(22), DELTA(2), RSAVE(20), RLIST(6),
   * R, DR, RCX, RCP, ENERGY
COMMON /CNLS/
   * NCHAN, NLAG, NBES, NMAX, NMAX2, LMAX, LMAX2, MMG, MNG, MXG,
   * NLF, NLG, NMS, NZG, NTOTAL, NFNEW, NLISTS, WFLEX, MLIST
C
DOUBLE PRECISION
   * WBES, RBES, D, AC, SIGMA, TAU, FC, GC, P, FBE5, GBE5, Y, V,
   * HA, HB, PHI, DELTA, RSAVE, RLIST, R, DR, RCX, RCP, ENERGY
C
301 FORMAT (1H1///35X,24HLIST OF INTERNAL ARRAYS,///)
302 FORMAT (///A6,18H ARRAY, LENGTH = 13,1H4)///)
303 FORMAT (2X,9113)
304 FORMAT (3H1,12,1H3), 9D13.4)
305 FORMAT (2H1,12,1H3), 9D13.4)
306 FORMAT (2H1,12,1H3), 9D13.4)
307 FORMAT (7H ZETA ,13,7H = ,12,1H3), 9D13.4)
C
WRITE (6,301)
C
D COEFFICIENTS
JTEMP = NLAG*NMAX
WRITE (6,302) WORD(I), JTEMP
WRITE (6,303) (M, M=1,NMAX)
DO 3005 I=1,NLAG
   J = (I-1)*NMAX
   JPLUS = J+1
JTEMP = NHASIS(I)-LBASIS(I)+J
WRITE (6,304) I, (DIM), M=JPLUS,JTEMP)
3005 CONTINUE

C WRITE (6,303) (M, M=2,NMAX2)
DO 3015 I=1,NLAG
ITEMP = (I*(I-1))/2
DO 3010 J=1,I
JTEMP = JITEMP+ITEMP
JPLUS = JTEMP-NMS+1
WRITE (6,305) I, J, (SIGMA(M), M=JPLUS,JTEMP)
3010 CONTINUE
3015 CONTINUE
C

AC COEFFICIENTS.
IF (JEXCH.EQ.0) GO TO 3030
JTEMP = (NLAG*(NLAG+1))/2
WRITE (6,302) WORD(2), JTEMP
DO 3025 I=1,NLAG
ITEMP = (I*(I-1))/2
DO 3020 J=1,I
JTEMP = JITEMP+ITEMP
WRITE (6,305) I, J, AC(JTEMP)
3020 CONTINUE
3025 CONTINUE
C

FC COEFFICIENTS.
3030 JTEMP = NLF*(NCHAN*(NCHAN+1))/2
WRITE (6,302) WORD(4), JTEMP
WRITE (6,303) (INDEX(M), M=1,NLF)
DO 3040 I=1,NCHAN
ITEMP = (I*(I-1))/2
DO 3035 J=1,I
JTEMP = JITEMP+ITEMP
JPLUS = JTEMP-NLF+1
WRITE (6,305) I, J, FC(M), J=JPLUS,JTEMP)
3035 CONTINUE
3040 CONTINUE
C

GC COEFFICIENTS.
IF (JEXCH.EQ.0) GO TO 3055
JTEMP = NLG*(NCHAN*(NCHAN+1))/2
WRITE (6,302) WORD(5), JTEMP
ITEMP = MNG+1
JTEMP = MNG+1
WRITE (6,303) (INDEX(M), M=ITEMP,JTEMP)
DO 3060 I=1,NCHAN
ITEMP = (I*(I-1))/2
DO 3055 J=1,I
JTEMP = JITEMP+NLG
JPLUS = JTEMP-NLG+1
WRITE (6,305) I, J, GC(M), M=JPLUS,JTEMP)
3055 CONTINUE
3060 CONTINUE
C

INDIC COEFFICIENTS.
3055 MTEMP = NLF*(NLAG*(NLAG+1))/2
WRITE (6,302) WORD(6), MTEMP
WRITE (6,303) (INDEX(M), M=1,NLF)
DO 3065 I=1,NLAG
ITEMP = (I*(I-1))/2
DO 3060 J=1,I
JTEMP = JITEMP+NLG
JPLUS = JTEMP-NLF+1
WRITE (6,306) I, J, (INDIC(M), M=JPLUS,JTEMP)
3060 CONTINUE
3065 CONTINUE
C

TAU COEFFICIENTS.
WRITE (6,302) WORD(7), MTEMP
WRITE (6,303) (INDEX(M), M=1,NLF)
DO 3075 I=1,NLAG
ITEMP = (I*I-I-1)/2
DO 3070 J=1,I
JTEMP = (J+ITEMP)*NL
JPLUS = JTEMP-NL+1
WRITE (6,305) I, J, (TAU(M), M=JPLUS,JTEMP)
3070 CONTINUE
3075 CONTINUE
C
C  ZETA SETS.
IF (JEXCH.EQ.0) RETURN
WRITE (6,302) WORD(I), NZG
DO 3080 I=1,NZG
WRITE (6,307) I, NZETA(I), NZZETA(I), LZETA(I)
3080 CONTINUE
RETURN
END

SUBROUTINE FFLIST
C
C THIS ROUTINE CAN BE USED TO LIST THE CALCULATED FUNCTIONS AT
C THE CURRENT COORDINATE R.
C
COMMON /IBLK/

C COMMON /DBLK/

C COMMON /CNRT/

C COMMON /INTL/

C COMMON /COUR/

C LOGICAL INDIC
C
C DOUBLE PRECISION
C
100 FORMAT (1H1/%13HFFSTR, R = ,F8.3)
101 FORMAT (//5X,17HRADIAL FUNCTIONS./,(5X,5(2X,I2,3M) =D16.9))
102 FORMAT (//5X,21HBESSEL FUNCTIONS./,(5X,5(2X,I2,3M) =D16.9))
103 FORMAT (//5X,21HBESSEL FUNCTIONS./,(5X,5(2X,I2,3M) =D16.9))
104 FORMAT (//5X,12HY INTEGRALS.)
105 FORMAT (//5X,12HY INTEGRALS.)
106 FORMAT (//5X,12HY INTEGRALS.)
107 FORMAT (//5X,4HPH1./(5X,5(2X,I2,3M) =D16.9))
C
WRITE (6,100) R
IF (R.GT.RCX) GO TO 1005
WRITE (6,101) (J,P(J),J=1,NLAG)
1005 WRITE (6,102) (I,FRESL(I),I=1,NBES)
WRITE (6,103) (I,FRESL(I),I=1,NBES)
WRITE (6,104)
DO 1010 I=1,NLAG
N = (I+1)/2
DO 1010 J=1,N
M = (J+N)*NL
L = M-NL+1
WRITE (6,105) I, J, (Y(K), K=L,M)
1010 CONTINUE
WRITE (6,106)
DO 1015 I=1,NCHAN
N = (I-1)*NCHAN
DO 1015 J=1,I
K = J+N
WRITE (6,105) I, J, V(K)
1015 CONTINUE
WRITE (6,107) (1,PHI(I),I=1,NTOTAL)
RETURN
END
Table I.
Labeling convention for the channel index $\nu = \{ n l_1 l_2 \}$

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>basis</th>
<th>ls-2s</th>
<th>ls-2s-2p</th>
<th>ls-2s-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>1 0 L</td>
<td>1 0 0</td>
<td>1 0 L</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2 0 L</td>
<td>2 0 0</td>
<td>2 0 L</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>2 1 1</td>
<td>2 1 L-1</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>2 1 L+1</td>
</tr>
</tbody>
</table>

L=0 | L>0
Table II.
The singlet L = 0 phase shift at E = 0.5 as a function of step size.a

<table>
<thead>
<tr>
<th>( \Delta )</th>
<th>phase shift</th>
<th>extrapolated phase shift</th>
<th>fractional error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.733776</td>
<td>0.7365746</td>
<td>-0.003799</td>
</tr>
<tr>
<td>0.05</td>
<td>0.7358574</td>
<td>0.7365566</td>
<td>-0.000949</td>
</tr>
<tr>
<td>0.025</td>
<td>0.7363819</td>
<td>0.7365567</td>
<td>-0.000237</td>
</tr>
<tr>
<td>0.0125</td>
<td>0.7365133</td>
<td>0.7365570</td>
<td>-0.000059</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.7365502</td>
<td>0.7365572</td>
<td>-0.000009</td>
</tr>
</tbody>
</table>

a Integration range is 15.

b Values extrapolated to zero step size by the Quadratic Rule.

c Error: \( \frac{[\delta(\Delta) - \delta(0)]}{\delta(0)} \)
Table III.

Some singlet $L = 0$ phase shifts calculated with various step sizes. For a given energy, the three rows give the results at $R_N = 10, 15, \text{ and } 20$. The Quadratic Rule coefficient $q$ is also shown.

<table>
<thead>
<tr>
<th>E</th>
<th>$\Delta = 0.1$</th>
<th>$\Delta = 0.05$</th>
<th>$\Delta = 0.01$</th>
<th>$\Delta = 0.005$</th>
<th>$\Delta = (0.0)^a$</th>
<th>q</th>
<th>$r(0.01)^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-0.7453009</td>
<td>-0.7432414</td>
<td>-0.7457735</td>
<td>-0.7457886</td>
<td>-0.3146</td>
<td>-0.000042</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.7475953</td>
<td>-0.7457507</td>
<td>-0.7457735</td>
<td>-0.2459</td>
<td>-0.000033</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.7476497</td>
<td>-0.7458072</td>
<td>-0.7457886</td>
<td>-0.1861</td>
<td>-0.000025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>1.5112680</td>
<td>1.5120067</td>
<td>1.5120506</td>
<td>1.5120375</td>
<td>-0.3078</td>
<td>-0.000020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5075490</td>
<td>1.5080758</td>
<td>1.5080923</td>
<td>1.5080978</td>
<td>-0.2195</td>
<td>-0.000015</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5075504</td>
<td>1.5080770</td>
<td>1.5080935</td>
<td>1.5080990</td>
<td>-0.2194</td>
<td>-0.000014</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.5396111</td>
<td>0.5438152</td>
<td>0.5438577</td>
<td>-0.4246</td>
<td>-0.000078</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5388178</td>
<td>0.5428601</td>
<td>0.5429009</td>
<td>-0.4083</td>
<td>-0.000075</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5388111</td>
<td>0.5428534</td>
<td>0.5428942</td>
<td>-0.4083</td>
<td>-0.000075</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Values extrapolated to zero step size by the Quadratic Rule.

$^b$ Fractional error in values calculated with $\Delta = 0.01$.  

Table IV.

Singlet and triplet phase shifts in the $1s$ exchange approximation.\(^a\)

In parentheses below each entry are values taken from Reference 2.

<table>
<thead>
<tr>
<th>$E$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s$</td>
<td>$t$</td>
<td>$s$</td>
</tr>
<tr>
<td>0.73</td>
<td>1.54752</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.548)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.73653</td>
<td>1.73868</td>
<td>-0.10848</td>
</tr>
<tr>
<td></td>
<td>(0.7370)</td>
<td>(1.739)</td>
<td>(-0.1084)</td>
</tr>
<tr>
<td>0.25</td>
<td>1.0308</td>
<td></td>
<td>-0.07030</td>
</tr>
<tr>
<td></td>
<td>(1.031)</td>
<td></td>
<td>(-0.0702)</td>
</tr>
<tr>
<td>0.09</td>
<td>1.508</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.508)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>1.87019</td>
<td>2.67915</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.871)</td>
<td>(2.679)</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>2.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2.396)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Singlet integration (0.01/15); triplet integration (0.01/15)(0.05/15).
Table V.

Results of calculations on four scattering states in the "strong coupling" exchange approximation showing dependence on step size. Integration schemes i. - v. are given in the text. For each $R$ matrix element or cross section, the three rows give the results at $R_N = 20$, $25$, and $30$. The number in parentheses is the power of ten by which the entries for that matrix element should be multiplied.
Table V.A.

Singlet L = 1 results at E = 0.81 for various integration schemes.\(^a\)

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme (i).</th>
<th>scheme (ii).</th>
<th>scheme (iii).</th>
<th>scheme (iv).</th>
<th>scheme (v).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{11}(0))</td>
<td>-0.103214</td>
<td>-0.103195</td>
<td>-0.103190</td>
<td>-0.103214</td>
<td>-0.103195</td>
</tr>
<tr>
<td></td>
<td>-0.103203</td>
<td>-0.103184</td>
<td>-0.103179</td>
<td>-0.103203</td>
<td>-0.103184</td>
</tr>
<tr>
<td>(R_{12}(-1))</td>
<td>-0.237618</td>
<td>-0.237536</td>
<td>-0.237515</td>
<td>-0.237614</td>
<td>-0.237536</td>
</tr>
<tr>
<td></td>
<td>-0.238100</td>
<td>-0.238021</td>
<td>-0.238001</td>
<td>-0.238090</td>
<td>-0.238018</td>
</tr>
<tr>
<td></td>
<td>-0.238125</td>
<td>-0.238046</td>
<td>-0.238026</td>
<td>-0.238115</td>
<td>-0.238043</td>
</tr>
<tr>
<td>(R_{22}(0))</td>
<td>-0.443408</td>
<td>-0.443417</td>
<td>-0.443419</td>
<td>-0.443427</td>
<td>-0.443422</td>
</tr>
<tr>
<td></td>
<td>-0.442613</td>
<td>-0.442624</td>
<td>-0.442627</td>
<td>-0.442629</td>
<td>-0.442627</td>
</tr>
<tr>
<td></td>
<td>-0.442417</td>
<td>-0.442426</td>
<td>-0.442429</td>
<td>-0.442436</td>
<td>-0.442431</td>
</tr>
<tr>
<td>(Q_{11}(-1))</td>
<td>0.388480</td>
<td>0.388341</td>
<td>0.388306</td>
<td>0.388480</td>
<td>0.388340</td>
</tr>
<tr>
<td></td>
<td>0.388395</td>
<td>0.388255</td>
<td>0.388220</td>
<td>0.388396</td>
<td>0.388255</td>
</tr>
<tr>
<td></td>
<td>0.388395</td>
<td>0.388255</td>
<td>0.388220</td>
<td>0.388396</td>
<td>0.388255</td>
</tr>
<tr>
<td>(Q_{12}(-2))</td>
<td>0.172764</td>
<td>0.172644</td>
<td>0.172613</td>
<td>0.172756</td>
<td>0.172644</td>
</tr>
<tr>
<td></td>
<td>0.173568</td>
<td>0.173451</td>
<td>0.173422</td>
<td>0.173551</td>
<td>0.173447</td>
</tr>
<tr>
<td></td>
<td>0.173629</td>
<td>0.173513</td>
<td>0.173484</td>
<td>0.173612</td>
<td>0.173508</td>
</tr>
</tbody>
</table>

\(^a\) See text.
Table V. B.

Triplet $L = 2$ results at $E = 1.00$ for various integration schemes.$^a$

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
<th>iv</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11} (-1)$</td>
<td>0.644974</td>
<td>0.644842</td>
<td>0.644809</td>
<td>0.644974</td>
<td>0.644842</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.644972</td>
<td>0.644839</td>
<td>0.644806</td>
<td>0.644972</td>
<td>0.644839</td>
<td></td>
</tr>
<tr>
<td>$R_{12} (-1)$</td>
<td>-0.673104</td>
<td>-0.672981</td>
<td>-0.672950</td>
<td>-0.673102</td>
<td>-0.672980</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.673102</td>
<td>-0.672979</td>
<td>-0.672948</td>
<td>-0.673100</td>
<td>-0.672978</td>
<td></td>
</tr>
<tr>
<td>$R_{22} (0)$</td>
<td>0.738862</td>
<td>0.738808</td>
<td>0.738795</td>
<td>0.738874</td>
<td>0.738812</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.738932</td>
<td>0.738879</td>
<td>0.738866</td>
<td>0.738942</td>
<td>0.738882</td>
<td></td>
</tr>
<tr>
<td>$Q_{11} (-1)$</td>
<td>0.578435</td>
<td>0.578206</td>
<td>0.578148</td>
<td>0.578434</td>
<td>0.578205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.578432</td>
<td>0.578203</td>
<td>0.578146</td>
<td>0.578432</td>
<td>0.578203</td>
<td></td>
</tr>
<tr>
<td>$Q_{12} (-1)$</td>
<td>0.435399</td>
<td>0.435264</td>
<td>0.435231</td>
<td>0.435391</td>
<td>0.435262</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.435336</td>
<td>0.435200</td>
<td>0.435166</td>
<td>0.435329</td>
<td>0.435198</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.435336</td>
<td>0.435200</td>
<td>0.435166</td>
<td>0.435328</td>
<td>0.435198</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ See text.
Table V.C.

Singlet $L = 1$ results at $E = 1.44$ for various integration schemes.\(^a\)

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>i.</th>
<th>ii.</th>
<th>iii.</th>
<th>iv.</th>
<th>v.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (-2)</td>
<td>-0.557670</td>
<td>-0.559668</td>
<td>-0.557616</td>
<td>-0.559658</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.558125</td>
<td>-0.560130</td>
<td>-0.558057</td>
<td>-0.560112</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.558079</td>
<td>-0.560082</td>
<td>-0.558013</td>
<td>-0.560066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-0.425844</td>
<td>-0.425564</td>
<td>-0.425848</td>
<td>-0.425564</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.425807</td>
<td>-0.425526</td>
<td>-0.425811</td>
<td>-0.425527</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.425810</td>
<td>-0.425529</td>
<td>-0.425814</td>
<td>-0.425530</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>.238408</td>
<td>.238282</td>
<td>.238410</td>
<td>.238282</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.238365</td>
<td>.238240</td>
<td>.238368</td>
<td>.238240</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.238367</td>
<td>.238241</td>
<td>.238370</td>
<td>.238242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (-1)</td>
<td>.111498</td>
<td>.111375</td>
<td>.111499</td>
<td>.111375</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.111505</td>
<td>.111381</td>
<td>.111505</td>
<td>.111381</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.111506</td>
<td>.111382</td>
<td>.111506</td>
<td>.111382</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td>.533281</td>
<td>.533070</td>
<td>.533281</td>
<td>.533070</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.533344</td>
<td>.533133</td>
<td>.533344</td>
<td>.533133</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.533346</td>
<td>.533135</td>
<td>.533346</td>
<td>.533135</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) See text.
Table V.D.

Singlet $L = 1$ results at $E = 2.25$ for various integration schemes.\textsuperscript{a}

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>ii.</th>
<th>iii.</th>
<th>iv.</th>
<th>v.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>i.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{11}$(-1)</td>
<td>0.507723</td>
<td>0.507707</td>
<td>0.507703</td>
<td>0.507722</td>
<td>0.507707</td>
</tr>
<tr>
<td></td>
<td>0.507728</td>
<td>0.507712</td>
<td>0.507709</td>
<td>0.507727</td>
<td>0.507712</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-0.350149</td>
<td>-0.349926</td>
<td>-0.349871</td>
<td>-0.350148</td>
<td>-0.349926</td>
</tr>
<tr>
<td></td>
<td>-0.350157</td>
<td>-0.349934</td>
<td>-0.349879</td>
<td>-0.350156</td>
<td>-0.349934</td>
</tr>
<tr>
<td></td>
<td>-0.350157</td>
<td>-0.349935</td>
<td>-0.349879</td>
<td>-0.350157</td>
<td>-0.349935</td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>0.173225</td>
<td>0.173243</td>
<td>0.173223</td>
<td>0.173243</td>
<td>0.173243</td>
</tr>
<tr>
<td></td>
<td>0.173245</td>
<td>0.173244</td>
<td>0.173223</td>
<td>0.173244</td>
<td>0.173244</td>
</tr>
<tr>
<td>$Q_{11}$(-2)</td>
<td>0.118351</td>
<td>0.118191</td>
<td>0.118152</td>
<td>0.118351</td>
<td>0.118192</td>
</tr>
<tr>
<td></td>
<td>0.118361</td>
<td>0.118202</td>
<td>0.118162</td>
<td>0.118362</td>
<td>0.118202</td>
</tr>
<tr>
<td>$Q_{12}$(-1)</td>
<td>0.384357</td>
<td>0.384153</td>
<td>0.384102</td>
<td>0.384358</td>
<td>0.384154</td>
</tr>
<tr>
<td></td>
<td>0.384373</td>
<td>0.384168</td>
<td>0.384118</td>
<td>0.384374</td>
<td>0.384169</td>
</tr>
<tr>
<td></td>
<td>0.384374</td>
<td>0.384169</td>
<td>0.384118</td>
<td>0.384374</td>
<td>0.384170</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See text.
Table VI.

Analysis of step size dependence of the results in Tables V.A. - V.D.

The first two columns give the changes in matrix elements $M$ calculated with step sizes $\Delta_x = 0.05$, $\Delta_y = 0.025$, and $\Delta_y = 0.0125$. The results of extrapolation to zero step size and the corresponding Quadratic Rule coefficients are shown. Also, the error due to finite step size $\Delta_y$ is evaluated. Rows a, b, c, d, and e correspond respectively to $R_{11}$, $R_{12}$, $R_{22}$, $Q_{11}$, and $Q_{12}$. Numbers in parentheses give the power of ten by which the matrix element differences and $M(0)$ should be multiplied.

<table>
<thead>
<tr>
<th>Table</th>
<th>$M(\Delta_x) - M(\Delta_y)$</th>
<th>$M(\Delta_y) - M(\Delta_y)$</th>
<th>$M(0)^a$</th>
<th>$q^b$</th>
<th>$f(\Delta_y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.A. a (0)</td>
<td>-0.000019</td>
<td>-0.000005</td>
<td>-0.103178</td>
<td>-0.101 (-1)</td>
<td>0.000061</td>
</tr>
<tr>
<td>b (-1)</td>
<td>-0.000079</td>
<td>-0.000020</td>
<td>-0.238020</td>
<td>-0.421 (-2)</td>
<td>0.000110</td>
</tr>
<tr>
<td>c (0)</td>
<td>0.000009</td>
<td>0.000003</td>
<td>-0.442429</td>
<td>0.48 (-2)</td>
<td>-0.000006</td>
</tr>
<tr>
<td>d (-1)</td>
<td>0.000140</td>
<td>0.000035</td>
<td>0.388208</td>
<td>0.747 (-2)</td>
<td>0.000120</td>
</tr>
<tr>
<td>e (-2)</td>
<td>0.000116</td>
<td>0.000029</td>
<td>0.173474</td>
<td>0.619 (-3)</td>
<td>0.000222</td>
</tr>
<tr>
<td>V.B. a (-1)</td>
<td>0.000133</td>
<td>0.000033</td>
<td>0.644795</td>
<td>0.709 (-2)</td>
<td>0.000068</td>
</tr>
<tr>
<td>b (-1)</td>
<td>-0.000123</td>
<td>-0.000031</td>
<td>-0.672938</td>
<td>-0.656 (-2)</td>
<td>0.000060</td>
</tr>
<tr>
<td>c (0)</td>
<td>0.000053</td>
<td>0.000013</td>
<td>0.738855</td>
<td>0.288 (-1)</td>
<td>0.000024</td>
</tr>
<tr>
<td>d (-1)</td>
<td>0.000229</td>
<td>0.000057</td>
<td>0.578127</td>
<td>0.122 (-1)</td>
<td>0.000132</td>
</tr>
<tr>
<td>e (-1)</td>
<td>0.000136</td>
<td>0.000034</td>
<td>0.435155</td>
<td>0.725 (-2)</td>
<td>0.000104</td>
</tr>
<tr>
<td>V.C. a (-2)</td>
<td>0.02003</td>
<td>-0.560750</td>
<td>0.107 (-1)</td>
<td>-0.00192</td>
<td></td>
</tr>
<tr>
<td>b (0)</td>
<td>-0.00281</td>
<td>-0.425435</td>
<td>-0.150 (0)</td>
<td>0.00220</td>
<td></td>
</tr>
<tr>
<td>c (+1)</td>
<td>0.00126</td>
<td>0.238199</td>
<td>0.672 (0)</td>
<td>0.00176</td>
<td></td>
</tr>
<tr>
<td>d (-1)</td>
<td>0.00124</td>
<td>0.11341</td>
<td>0.661 (-2)</td>
<td>0.000371</td>
<td></td>
</tr>
<tr>
<td>e (-1)</td>
<td>0.00211</td>
<td>0.533065</td>
<td>0.112 (-1)</td>
<td>0.000131</td>
<td></td>
</tr>
<tr>
<td>V.D. a (-1)</td>
<td>0.000016</td>
<td>0.000003</td>
<td>0.507072</td>
<td>0.85 (-3)</td>
<td>0.00010</td>
</tr>
<tr>
<td>b (0)</td>
<td>-0.00222</td>
<td>-0.000056</td>
<td>-0.349861</td>
<td>-0.118 (0)</td>
<td>0.00211</td>
</tr>
<tr>
<td>c (+1)</td>
<td>0.00081</td>
<td>0.00021</td>
<td>0.173217</td>
<td>0.432 (0)</td>
<td>0.00155</td>
</tr>
<tr>
<td>d (-2)</td>
<td>0.00159</td>
<td>0.00040</td>
<td>0.118150</td>
<td>0.848 (-3)</td>
<td>0.000448</td>
</tr>
<tr>
<td>e (-1)</td>
<td>0.00205</td>
<td>0.000041</td>
<td>0.384101</td>
<td>0.109 (-1)</td>
<td>0.000177</td>
</tr>
</tbody>
</table>

a Value extrapolated to zero step size by Eq. (1.42) of text.

b Numbers in parentheses give the power of ten by which the preceding number should be multiplied.
Table VII.

Singlet and triplet $L=0$ results in the $ls-2s$ exchange approximation, calculated with integration scheme v.' (see text), showing dependence on range of integration. The first five columns give the actual matrix elements at each $R_N$. The last three columns give the fractional changes in each matrix element for integration over the range indicated. Rows a, b, c, d, and e correspond respectively to $R_{11}$, $R_{12}$, $R_{22}$, $Q_{11}$, and $Q_{12}$. Numbers in parentheses give the power of ten by which the matrix elements in that row should be multiplied.
Table VII.A.

Singlet $L = 0$ results at various energies showing dependence on range of integration.

<table>
<thead>
<tr>
<th>E</th>
<th>$R_N = 20$</th>
<th>$R_N = 25$</th>
<th>$R_N = 30$</th>
<th>$R_N = 35$</th>
<th>$R_N = 40$</th>
<th>fractional changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 - 30</td>
</tr>
<tr>
<td>0.81</td>
<td>a (0)</td>
<td>1.28088</td>
<td>0.779028</td>
<td>0.776638</td>
<td>0.776718</td>
<td>0.776699</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>0.340080</td>
<td>0.231148</td>
<td>0.231999</td>
<td>0.232058</td>
<td>0.232044</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.199640</td>
<td>0.159320</td>
<td>0.160551</td>
<td>0.160968</td>
<td>0.160980</td>
</tr>
<tr>
<td></td>
<td>d (0)</td>
<td>0.699221</td>
<td>0.533117</td>
<td>0.531124</td>
<td>0.531154</td>
<td>0.531144</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.487075</td>
<td>0.378196</td>
<td>0.381536</td>
<td>0.381652</td>
<td>0.381615</td>
</tr>
<tr>
<td>1.00</td>
<td>a (0)</td>
<td>0.615737</td>
<td>0.596671</td>
<td>0.589331</td>
<td>0.589918</td>
<td>0.589923</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>0.426741</td>
<td>0.437045</td>
<td>0.454638</td>
<td>0.454648</td>
<td>0.454493</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>-0.767594</td>
<td>-0.801095</td>
<td>-0.801584</td>
<td>-0.801616</td>
<td>-0.801642</td>
</tr>
<tr>
<td></td>
<td>d (0)</td>
<td>-0.292558</td>
<td>0.286706</td>
<td>0.282591</td>
<td>0.282563</td>
<td>0.282570</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>-0.659515</td>
<td>0.723466</td>
<td>0.721257</td>
<td>0.720837</td>
<td>0.720878</td>
</tr>
<tr>
<td>1.44</td>
<td>a (0)</td>
<td>0.626415</td>
<td>0.361868</td>
<td>0.361732</td>
<td>0.000376</td>
<td>0.002853</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>0.989325</td>
<td>0.633851</td>
<td>0.632048</td>
<td>0.000376</td>
<td>0.002853</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>0.101293</td>
<td>0.149520</td>
<td>0.150072</td>
<td>0.000376</td>
<td>0.002853</td>
</tr>
<tr>
<td></td>
<td>d (0)</td>
<td>0.298059</td>
<td>0.139997</td>
<td>0.139555</td>
<td>0.000376</td>
<td>0.002853</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.979375</td>
<td>0.551498</td>
<td>0.547180</td>
<td>0.000376</td>
<td>0.002853</td>
</tr>
<tr>
<td>2.25</td>
<td>a (0)</td>
<td>0.195652</td>
<td>0.188387</td>
<td>0.195715</td>
<td>0.194410</td>
<td>0.194528</td>
</tr>
<tr>
<td></td>
<td>b (1)</td>
<td>0.119491</td>
<td>0.121476</td>
<td>0.125161</td>
<td>0.125483</td>
<td>0.125477</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>-0.508673</td>
<td>-0.439983</td>
<td>-0.435568</td>
<td>-0.436140</td>
<td>-0.436233</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.736228</td>
<td>0.829183</td>
<td>0.902825</td>
<td>0.902777</td>
<td>0.902839</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.178054</td>
<td>0.228866</td>
<td>0.240124</td>
<td>0.240677</td>
<td>0.240558</td>
</tr>
<tr>
<td>E</td>
<td>RN = 20</td>
<td>RN = 25</td>
<td>RN = 30</td>
<td>RN = 35</td>
<td>RN = 40</td>
<td>fractional changes</td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>0.81</td>
<td>a (2) -0.074101</td>
<td>0.136986</td>
<td>0.136797</td>
<td>0.137170</td>
<td>0.137163</td>
<td>0.001382 0.002719 0.000051</td>
</tr>
<tr>
<td></td>
<td>b (0) -3.37971</td>
<td>0.377006</td>
<td>0.495538</td>
<td>0.506234</td>
<td>0.595607</td>
<td>0.239199 0.021128 0.001240</td>
</tr>
<tr>
<td></td>
<td>c (1) 0.042664</td>
<td>0.255325</td>
<td>0.336782</td>
<td>0.337134</td>
<td>0.337103</td>
<td>0.241869 0.001044 0.000092</td>
</tr>
<tr>
<td></td>
<td>d (1) 0.339856</td>
<td>0.368319</td>
<td>0.368304</td>
<td>0.368311</td>
<td>0.368311</td>
<td>0.000041 0.000019 0.000002</td>
</tr>
<tr>
<td></td>
<td>e (-3) 145.067</td>
<td>0.373652</td>
<td>0.395437</td>
<td>0.409832</td>
<td>0.408921</td>
<td>0.055091 0.053124 0.002228</td>
</tr>
<tr>
<td></td>
<td>a (1) 0.662678</td>
<td>0.554683</td>
<td>0.559540</td>
<td>0.559733</td>
<td>0.559734</td>
<td>0.008680 0.000345 0.000002</td>
</tr>
<tr>
<td></td>
<td>b (0) 2.29999</td>
<td>0.203393</td>
<td>0.153519</td>
<td>0.153829</td>
<td>0.153812</td>
<td>0.197721 0.001221 0.000110</td>
</tr>
<tr>
<td></td>
<td>c (-1) 4.18567</td>
<td>0.202045</td>
<td>0.428915</td>
<td>0.428590</td>
<td>0.428307</td>
<td>0.528939 0.00758 0.000661</td>
</tr>
<tr>
<td></td>
<td>d (1) 0.243121</td>
<td>0.289799</td>
<td>0.290288</td>
<td>0.290293</td>
<td>0.290293</td>
<td>0.001684 0.000017 0.000002</td>
</tr>
<tr>
<td></td>
<td>e (-2) 25.5964</td>
<td>0.389591</td>
<td>0.218194</td>
<td>0.218929</td>
<td>0.218880</td>
<td>0.785526 0.003357 0.002224</td>
</tr>
<tr>
<td>1.00</td>
<td>a (1) 0.448978</td>
<td>0.271677</td>
<td>0.272704</td>
<td></td>
<td></td>
<td>0.003766</td>
</tr>
<tr>
<td></td>
<td>b (0) -2.80594</td>
<td>0.244802</td>
<td>0.221472</td>
<td></td>
<td></td>
<td>0.105341</td>
</tr>
<tr>
<td></td>
<td>c (0) 0.701752</td>
<td>-0.978897</td>
<td>-0.969555</td>
<td></td>
<td></td>
<td>0.009635</td>
</tr>
<tr>
<td></td>
<td>d (1) 0.148122</td>
<td>0.182646</td>
<td>0.182494</td>
<td></td>
<td></td>
<td>0.001656</td>
</tr>
<tr>
<td></td>
<td>e (-2) 27.4964</td>
<td>0.740776</td>
<td>0.610892</td>
<td></td>
<td></td>
<td>0.212614</td>
</tr>
<tr>
<td>1.44</td>
<td>a (1) 0.448978</td>
<td>0.271677</td>
<td>0.272704</td>
<td></td>
<td></td>
<td>0.003766</td>
</tr>
<tr>
<td></td>
<td>b (0) -2.80594</td>
<td>0.244802</td>
<td>0.221472</td>
<td></td>
<td></td>
<td>0.105341</td>
</tr>
<tr>
<td></td>
<td>c (0) 0.701752</td>
<td>-0.978897</td>
<td>-0.969555</td>
<td></td>
<td></td>
<td>0.009635</td>
</tr>
<tr>
<td></td>
<td>d (1) 0.148122</td>
<td>0.182646</td>
<td>0.182494</td>
<td></td>
<td></td>
<td>0.001656</td>
</tr>
<tr>
<td></td>
<td>e (-2) 27.4964</td>
<td>0.740776</td>
<td>0.610892</td>
<td></td>
<td></td>
<td>0.212614</td>
</tr>
<tr>
<td>2.25</td>
<td>a (1) 0.079144</td>
<td>0.157048</td>
<td>0.160216</td>
<td>0.160163</td>
<td>0.160192</td>
<td>0.019773 0.003311 0.000181</td>
</tr>
<tr>
<td></td>
<td>b (0) 1.67537</td>
<td>0.599638</td>
<td>0.475516</td>
<td>0.477547</td>
<td>0.473308</td>
<td>0.261026 0.004253 0.001501</td>
</tr>
<tr>
<td></td>
<td>c (1) -0.617490</td>
<td>-0.355805</td>
<td>-0.325781</td>
<td>-0.325360</td>
<td>-0.325120</td>
<td>0.086159 0.006826 0.000738</td>
</tr>
<tr>
<td></td>
<td>d (0) 0.762811</td>
<td>0.966178</td>
<td>0.970092</td>
<td>0.970022</td>
<td>0.970128</td>
<td>0.004035 0.000093 0.000130</td>
</tr>
<tr>
<td></td>
<td>e (-2) 3.57907</td>
<td>0.918129</td>
<td>0.674162</td>
<td>0.688073</td>
<td>0.690846</td>
<td>0.361882 0.020217 0.004014</td>
</tr>
</tbody>
</table>
Table VIII.

Singlet and triplet results for \( L > 0 \) in the 1s-2s exchange approximation, calculated with integration scheme v. (see text), showing dependence on range of integration. The first three columns give the actual matrix elements at each \( R_N \). The last column gives the fractional change in each matrix element for integration over the range indicated. Rows a, b, c, d, and e have the same meaning as before. Numbers in parentheses give the power of ten by which matrix elements in that row should be multiplied.
Table VIII.A.

Singlet results at various energies showing dependence on the range of integration.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>1 a</td>
<td>-0.103195</td>
<td>-0.103184</td>
<td>-0.103184</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>b (-1)</td>
<td>0.237536</td>
<td>-0.238018</td>
<td>-0.238043</td>
<td>.000105</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>-0.143422</td>
<td>-0.442627</td>
<td>-0.442431</td>
<td>.000443</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.388240</td>
<td>0.388255</td>
<td>0.388255</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>e (-2)</td>
<td>0.172644</td>
<td>0.173417</td>
<td>0.173508</td>
<td>.000352</td>
</tr>
<tr>
<td>2.00</td>
<td>1 a</td>
<td>-0.162373</td>
<td>-0.162373</td>
<td>-0.162373</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b (-3)</td>
<td>0.286471</td>
<td>0.286238</td>
<td>0.286286</td>
<td>0.00168</td>
</tr>
<tr>
<td></td>
<td>c (-1)</td>
<td>-0.561766</td>
<td>-0.564028</td>
<td>-0.563848</td>
<td>0.000319</td>
</tr>
<tr>
<td></td>
<td>d (-2)</td>
<td>0.162703</td>
<td>0.162703</td>
<td>0.162703</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>e (-6)</td>
<td>0.504851</td>
<td>0.504017</td>
<td>0.504186</td>
<td>.000335</td>
</tr>
<tr>
<td>1.44</td>
<td>1 a</td>
<td>-0.170499</td>
<td>-0.170499</td>
<td>-0.170499</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b (-2)</td>
<td>0.640315</td>
<td>0.640460</td>
<td>0.640474</td>
<td>0.00022</td>
</tr>
<tr>
<td></td>
<td>c (-1)</td>
<td>0.371480</td>
<td>0.370296</td>
<td>0.370362</td>
<td>0.00178</td>
</tr>
<tr>
<td></td>
<td>d (-2)</td>
<td>0.145323</td>
<td>0.145322</td>
<td>0.145322</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>e (-3)</td>
<td>0.204643</td>
<td>0.204737</td>
<td>0.204746</td>
<td>0.00044</td>
</tr>
<tr>
<td>2.25</td>
<td>1 a</td>
<td>-0.125755</td>
<td>-0.125755</td>
<td>-0.125755</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b (-1)</td>
<td>-0.462536</td>
<td>-0.462527</td>
<td>-0.462530</td>
<td>0.00007</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.238282</td>
<td>0.238240</td>
<td>0.238242</td>
<td>0.00008</td>
</tr>
<tr>
<td></td>
<td>d (-3)</td>
<td>0.643284</td>
<td>0.643285</td>
<td>0.643285</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>e (-2)</td>
<td>0.541961</td>
<td>0.541968</td>
<td>0.541968</td>
<td>0</td>
</tr>
<tr>
<td>2.50</td>
<td>1 a</td>
<td>0.507707</td>
<td>0.507712</td>
<td>0.507712</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>0.349926</td>
<td>0.349934</td>
<td>0.349935</td>
<td>0.00003</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>0.173243</td>
<td>0.173244</td>
<td>0.173243</td>
<td>0.00006</td>
</tr>
<tr>
<td></td>
<td>d (-2)</td>
<td>0.118202</td>
<td>0.118202</td>
<td>0.118203</td>
<td>0.00008</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.384154</td>
<td>0.384169</td>
<td>0.384170</td>
<td>0.00003</td>
</tr>
<tr>
<td>2.50</td>
<td>2 a</td>
<td>0.408548</td>
<td>0.408548</td>
<td>0.408548</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b (-2)</td>
<td>0.893184</td>
<td>0.893182</td>
<td>0.893183</td>
<td>0.00001</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.773852</td>
<td>0.773851</td>
<td>0.773850</td>
<td>0.00001</td>
</tr>
<tr>
<td></td>
<td>d (-4)</td>
<td>0.548894</td>
<td>0.548894</td>
<td>0.548894</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>1.09784</td>
<td>1.09784</td>
<td>1.09784</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table VIII.B.

Triplet results at various energies showing dependence on the range of integration.

<table>
<thead>
<tr>
<th>Energy</th>
<th>( L )</th>
<th>( R_N = 20 )</th>
<th>( R_N = 25 )</th>
<th>( R_N = 30 )</th>
<th>Fractional change 25 - 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>1</td>
<td>0.346894</td>
<td>0.346837</td>
<td>0.346840</td>
<td>0.000009</td>
</tr>
<tr>
<td></td>
<td>a (0)</td>
<td>0.346894</td>
<td>0.346837</td>
<td>0.346840</td>
<td>0.000009</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>0.306477</td>
<td>0.305854</td>
<td>0.306557</td>
<td>0.000688</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>-0.208097</td>
<td>-0.208129</td>
<td>-0.208124</td>
<td>0.000024</td>
</tr>
<tr>
<td></td>
<td>d (1)</td>
<td>0.138766</td>
<td>0.138742</td>
<td>0.138741</td>
<td>0.000007</td>
</tr>
<tr>
<td></td>
<td>e (0)</td>
<td>0.167598</td>
<td>0.167673</td>
<td>0.167652</td>
<td>0.000125</td>
</tr>
<tr>
<td></td>
<td>a (-1)</td>
<td>0.501384</td>
<td>0.501379</td>
<td>0.501380</td>
<td>0.000002</td>
</tr>
<tr>
<td></td>
<td>b (-1)</td>
<td>-0.180134</td>
<td>-0.180100</td>
<td>-0.180094</td>
<td>0.000033</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.178407</td>
<td>0.178569</td>
<td>0.178539</td>
<td>0.000168</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.463053</td>
<td>0.463045</td>
<td>0.463046</td>
<td>0.000002</td>
</tr>
<tr>
<td></td>
<td>e (-2)</td>
<td>0.580540</td>
<td>0.580285</td>
<td>0.580256</td>
<td>0.000050</td>
</tr>
<tr>
<td>1.00</td>
<td>1</td>
<td>0.612004</td>
<td>0.612680</td>
<td>0.612647</td>
<td>0.000054</td>
</tr>
<tr>
<td></td>
<td>a (0)</td>
<td>0.612004</td>
<td>0.612680</td>
<td>0.612647</td>
<td>0.000054</td>
</tr>
<tr>
<td></td>
<td>b (1)</td>
<td>-0.155363</td>
<td>-0.155788</td>
<td>-0.155766</td>
<td>0.000141</td>
</tr>
<tr>
<td></td>
<td>c (2)</td>
<td>0.108888</td>
<td>0.109152</td>
<td>0.109138</td>
<td>0.000128</td>
</tr>
<tr>
<td></td>
<td>d (1)</td>
<td>0.116186</td>
<td>0.116183</td>
<td>1.116183</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>e (0)</td>
<td>0.152092</td>
<td>0.152190</td>
<td>0.152186</td>
<td>0.000026</td>
</tr>
<tr>
<td></td>
<td>a (-1)</td>
<td>0.644842</td>
<td>0.644839</td>
<td>0.644839</td>
<td>0.000003</td>
</tr>
<tr>
<td></td>
<td>b (-1)</td>
<td>-0.672980</td>
<td>-0.672978</td>
<td>-0.672978</td>
<td>0.000003</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.738812</td>
<td>0.738882</td>
<td>0.738876</td>
<td>0.000008</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.578205</td>
<td>0.578203</td>
<td>0.578203</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.435262</td>
<td>0.435198</td>
<td>0.435198</td>
<td>0.000000</td>
</tr>
<tr>
<td>1.44</td>
<td>1</td>
<td>0.436939</td>
<td>0.436937</td>
<td>0.436937</td>
<td>0.000010</td>
</tr>
<tr>
<td></td>
<td>a (0)</td>
<td>0.436939</td>
<td>0.436937</td>
<td>0.436937</td>
<td>0.000010</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>-0.411257</td>
<td>-0.411274</td>
<td>-0.411270</td>
<td>0.000006</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>0.334126</td>
<td>0.334177</td>
<td>0.334175</td>
<td>0.000006</td>
</tr>
<tr>
<td></td>
<td>d (0)</td>
<td>0.808051</td>
<td>0.808050</td>
<td>0.808056</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.736158</td>
<td>0.736019</td>
<td>0.736010</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>a (-1)</td>
<td>0.868578</td>
<td>0.868578</td>
<td>0.868578</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>b (-1)</td>
<td>-0.970598</td>
<td>-0.970594</td>
<td>-0.970593</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.827165</td>
<td>0.827162</td>
<td>0.827161</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.695129</td>
<td>0.695130</td>
<td>0.695130</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.572366</td>
<td>0.572363</td>
<td>0.572363</td>
<td>0.000001</td>
</tr>
<tr>
<td>2.25</td>
<td>1</td>
<td>0.395614</td>
<td>0.395613</td>
<td>0.395613</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>a (0)</td>
<td>0.395614</td>
<td>0.395613</td>
<td>0.395613</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>-0.226078</td>
<td>-0.226069</td>
<td>-0.226069</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>c (1)</td>
<td>0.199221</td>
<td>0.199221</td>
<td>0.199221</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>d (0)</td>
<td>0.485010</td>
<td>0.485012</td>
<td>0.485012</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.354271</td>
<td>0.354245</td>
<td>0.354244</td>
<td>0.000003</td>
</tr>
<tr>
<td></td>
<td>a (0)</td>
<td>0.110352</td>
<td>0.110352</td>
<td>0.110352</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>b (0)</td>
<td>-0.102412</td>
<td>-0.102412</td>
<td>-0.102412</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>c (0)</td>
<td>0.827313</td>
<td>0.827314</td>
<td>0.827314</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>d (-1)</td>
<td>0.723363</td>
<td>0.723363</td>
<td>0.723363</td>
<td>0.000001</td>
</tr>
<tr>
<td></td>
<td>e (-1)</td>
<td>0.405549</td>
<td>0.405549</td>
<td>0.405549</td>
<td>0.000001</td>
</tr>
</tbody>
</table>
Table IX.

Results of calculations on singlet $L = 0$ state at $\xi = 0.81$ in the $1s$-$2s$-$2p$ exchange approximation showing dependence on step size. Integration schemes i.-iii. are given in the text. For each matrix element, the number in parentheses gives the power of ten by which the entries in that row should be multiplied.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>i.</th>
<th>ii.</th>
<th>iii.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (0)</td>
<td></td>
<td>0.827329</td>
<td>0.828295</td>
<td>0.828537</td>
</tr>
<tr>
<td>$R_{12}$ (-1)</td>
<td></td>
<td>-0.726421</td>
<td>-0.726310</td>
<td>-0.726282</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td></td>
<td>0.666539</td>
<td>0.666535</td>
<td>0.666585</td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td></td>
<td>-0.325241</td>
<td>-0.325259</td>
<td>-0.325263</td>
</tr>
<tr>
<td>$R_{33}$ (+1)</td>
<td></td>
<td>0.136943</td>
<td>0.136946</td>
<td>0.136947</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td></td>
<td>-0.115110</td>
<td>-0.115333</td>
<td>-0.115388</td>
</tr>
<tr>
<td>$Q_{11}$ (0)</td>
<td></td>
<td>0.446142</td>
<td>0.446743</td>
<td>0.446894</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td></td>
<td>0.600150</td>
<td>0.599952</td>
<td>0.599902</td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td></td>
<td>0.333907</td>
<td>0.333800</td>
<td>0.333773</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td></td>
<td>0.577139</td>
<td>0.577139</td>
<td>0.577140</td>
</tr>
</tbody>
</table>
Table X.

Analysis of step size dependence of the results in Table IX. The first two columns give the changes in matrix elements $M$ calculated with step sizes $\Delta_\alpha = 0.05$, $\Delta_\beta = 0.025$, and $\Delta_\gamma = 0.0125$. The results of extrapolation to zero step size and the corresponding Quadratic Rule coefficients are shown. Also, the error due to finite step size $\Delta_\beta$ is evaluated. The numbers in parentheses give the power of ten by which the matrix element differences and $M(0)$ should be multiplied.

<table>
<thead>
<tr>
<th>matrix element $M$</th>
<th>$M(\Delta_\alpha)-M(\Delta_\beta)$</th>
<th>$M(\Delta_\beta)-M(\Delta_\gamma)$</th>
<th>$M(0)^a$</th>
<th>$q^b$</th>
<th>$f(\Delta_\beta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (0)</td>
<td>-0.000966</td>
<td>-0.000242</td>
<td>0.828617</td>
<td>-0.515 (0)</td>
<td>-0.000388</td>
</tr>
<tr>
<td>$R_{12}$ (-1)</td>
<td>-0.000111</td>
<td>-0.000028</td>
<td>-0.726273</td>
<td>-0.592 (-2)</td>
<td>0.000051</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>-0.000196</td>
<td>-0.000050</td>
<td>0.666600</td>
<td>-0.104 (0)</td>
<td>-0.000098</td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td>0.000018</td>
<td>0.000004</td>
<td>-0.325265</td>
<td>0.96 (-2)</td>
<td>-0.000018</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>-0.000003</td>
<td>-0.000001</td>
<td>0.1369147</td>
<td>-0.16 (-1)</td>
<td>-0.000007</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>0.000223</td>
<td>0.000055</td>
<td>-0.115407</td>
<td>0.119 (0)</td>
<td>-0.000644</td>
</tr>
<tr>
<td>$Q_{11}$ (0)</td>
<td>-0.000601</td>
<td>-0.000151</td>
<td>0.446943</td>
<td>-0.320 (0)</td>
<td>-0.000448</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td>0.000198</td>
<td>0.000050</td>
<td>0.599886</td>
<td>0.106 (-1)</td>
<td>0.000110</td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td>0.000107</td>
<td>0.000027</td>
<td>0.333764</td>
<td>0.571 (-2)</td>
<td>0.000106</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.0</td>
<td>-0.000001</td>
<td>0.577139</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ Value extrapolated to zero step size by Eq. (1.42) of text.

$^b$ Numbers in parentheses give the power of ten by which the preceding number should be multiplied.
Table XI.

Results from two calculations on the singlet \( L = 0 \) state at \( E = 1.00 \) in the 1s-2s-2p exchange approximation, using different values of the exponential cutoff coordinate. Both integrations were done with \((0.025/30)(0.25/60)\). The first two columns are the actual results of integration to \( R_N = 60 \), with the indicated cutoff. The next two columns are the results of the projection procedure applied at \( R_N = 60 \). The "BSS" column are results from Reference 5. For each matrix element, the number in parentheses gives the power of ten by which all entries in that row should be multiplied.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>cutoff</th>
<th>30</th>
<th>40</th>
<th>30 (projected)</th>
<th>40 (projected)</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} ) (0)</td>
<td>0.299060</td>
<td>0.299260</td>
<td>0.292167</td>
<td>0.292371</td>
<td>0.2891</td>
<td></td>
</tr>
<tr>
<td>( R_{12} ) (0)</td>
<td>0.168815</td>
<td>0.169021</td>
<td>-0.003762</td>
<td>-0.003503</td>
<td>-0.0059</td>
<td></td>
</tr>
<tr>
<td>( R_{13} ) (+1)</td>
<td>0.166425</td>
<td>0.166375</td>
<td>0.169059</td>
<td>0.169011</td>
<td>0.17014</td>
<td></td>
</tr>
<tr>
<td>( R_{22} ) (0)</td>
<td>0.259780</td>
<td>0.259962</td>
<td>0.020597</td>
<td>0.020928</td>
<td>0.0184</td>
<td></td>
</tr>
<tr>
<td>( R_{23} ) (-1)</td>
<td>0.088651</td>
<td>0.088575</td>
<td>0.147359</td>
<td>0.147290</td>
<td>0.14779</td>
<td></td>
</tr>
<tr>
<td>( R_{33} ) (+1)</td>
<td>-0.564245</td>
<td>-0.564291</td>
<td>-0.550806</td>
<td>-0.550868</td>
<td>-0.55243</td>
<td></td>
</tr>
<tr>
<td>( Q_{11} ) (0)</td>
<td>0.264178</td>
<td>0.264165</td>
<td>0.264599</td>
<td>0.264586</td>
<td>0.2635</td>
<td></td>
</tr>
<tr>
<td>( Q_{12} ) (-1)</td>
<td>0.763400</td>
<td>0.763212</td>
<td>0.760486</td>
<td>0.760299</td>
<td>0.766</td>
<td></td>
</tr>
<tr>
<td>( Q_{13} ) (-1)</td>
<td>0.367272</td>
<td>0.367109</td>
<td>0.356480</td>
<td>0.356320</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>( Q_{22} ) (0)</td>
<td>0.300997</td>
<td>0.301001</td>
<td>0.288131</td>
<td>0.288125</td>
<td>0.2876</td>
<td></td>
</tr>
</tbody>
</table>
Table XII.

Results of calculations on the singlet L = 0 state at E = 0.81 showing dependence on step size in the outer region. Integration schemes are given in the text. The first two columns give the actual results of the integration scheme. The next two columns are the results of the projection procedure applied at $R_N = 200$. The fractional difference in the calculated matrix elements is given in the last column. The number in parentheses gives the power of ten by which each matrix element in that row should be multiplied.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>iv.</th>
<th>v.</th>
<th>iv. (projected)</th>
<th>v. (projected)</th>
<th>fractional error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (0)</td>
<td></td>
<td>0.823202</td>
<td>0.823203</td>
<td>0.823026</td>
<td>0.823027</td>
<td>0.000001</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td></td>
<td>-0.239346</td>
<td>-0.239339</td>
<td>-0.275476</td>
<td>-0.275469</td>
<td>-0.000029</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td></td>
<td>0.605860</td>
<td>0.605863</td>
<td>0.588615</td>
<td>0.588619</td>
<td>0.000005</td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td></td>
<td>-0.970678</td>
<td>-0.970650</td>
<td>-1.10141</td>
<td>-1.10139</td>
<td>-0.000029</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td></td>
<td>0.111872</td>
<td>0.111872</td>
<td>0.102150</td>
<td>0.102150</td>
<td>0.000000</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td></td>
<td>0.457615</td>
<td>0.457646</td>
<td>0.588418</td>
<td>0.588450</td>
<td>0.000068</td>
</tr>
<tr>
<td>$Q_{11}$ (0)</td>
<td></td>
<td>0.449078</td>
<td>0.449077</td>
<td>0.448958</td>
<td>0.448956</td>
<td>0.000002</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td></td>
<td>0.541433</td>
<td>0.541439</td>
<td>0.528206</td>
<td>0.528212</td>
<td>0.000011</td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td></td>
<td>0.375540</td>
<td>0.375538</td>
<td>0.385846</td>
<td>0.385844</td>
<td>0.000005</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td></td>
<td>0.722049</td>
<td>0.722047</td>
<td>0.783094</td>
<td>0.783096</td>
<td>0.000003</td>
</tr>
</tbody>
</table>
Table XIII.

Singlet $L = 0$, three channel results, calculated in the $1s$-$2s$-$2p$ approximation by integration scheme $v$. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BSS" column contains values from Reference 5.
Table XIII.A.
Singlet $L = 0$ results at $E = 0.81$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (0)</td>
<td>0.828954</td>
<td>0.823314</td>
<td>0.823203</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.826109</td>
<td>0.823026</td>
<td>0.823027</td>
<td>0.8189</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-0.072214</td>
<td>-0.213177</td>
<td>-0.239339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.254104</td>
<td>-0.274404</td>
<td>-0.275469</td>
<td>-0.2763</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>0.663341</td>
<td>0.615052</td>
<td>0.605863</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.571152</td>
<td>0.586805</td>
<td>0.588619</td>
<td>0.5863</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>-0.032633</td>
<td>-0.087266</td>
<td>-0.097065</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.106496</td>
<td>-0.110061</td>
<td>-0.110139</td>
<td>-0.10994</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>0.136553</td>
<td>0.117474</td>
<td>0.111872</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.104333</td>
<td>0.102176</td>
<td>0.102150</td>
<td>0.10211</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>-0.102574</td>
<td>0.369834</td>
<td>0.457646</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.573328</td>
<td>0.588280</td>
<td>0.588450</td>
<td>0.5841</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (0)</td>
<td>0.446805</td>
<td>0.448904</td>
<td>0.449077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.449105</td>
<td>0.448928</td>
<td>0.448956</td>
<td>0.4474</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td>0.596278</td>
<td>0.548282</td>
<td>0.541439</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.489881</td>
<td>0.524896</td>
<td>0.528212</td>
<td>0.529</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td>0.333178</td>
<td>0.366988</td>
<td>0.375538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.355836</td>
<td>0.383376</td>
<td>0.385844</td>
<td>0.384</td>
<td></td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.577481</td>
<td>0.684493</td>
<td>0.722047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.768260</td>
<td>0.782759</td>
<td>0.783090</td>
<td>0.78183</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.085772</td>
<td>0.010222</td>
<td>0.003710</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XIII.B.

Singlet $L = 0$ results at $E = 1.00$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.318620</td>
<td>0.294941</td>
<td>0.293366</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.292199</td>
<td>0.292535</td>
<td>0.292484</td>
<td>0.2891</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>2.59161</td>
<td>.831913</td>
<td>.474764</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>-.392006</td>
<td>-.383601</td>
<td>-.392234</td>
<td>-.59</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(+1)</td>
<td>.160384</td>
<td>.168906</td>
<td>.169520</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.168093</td>
<td>.169567</td>
<td>.169724</td>
<td>.17014</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>.336420</td>
<td>.155621</td>
<td>.103916</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.199830</td>
<td>.204080</td>
<td>.202886</td>
<td>.184</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(+1)</td>
<td>.057258</td>
<td>.118453</td>
<td>.130493</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.147436</td>
<td>.147392</td>
<td>.147427</td>
<td>.14779</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>-.559665</td>
<td>-.562111</td>
<td>-.558684</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-.550810</td>
<td>-.550702</td>
<td>-.550844</td>
<td>-.55243</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(0)</td>
<td>.264460</td>
<td>.264610</td>
<td>.264595</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.264522</td>
<td>.264571</td>
<td>.264570</td>
<td>.2635</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>.762343</td>
<td>.765798</td>
<td>.766618</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.751247</td>
<td>.765810</td>
<td>.767000</td>
<td>.766</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-1)</td>
<td>.365899</td>
<td>.361562</td>
<td>.360456</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.352654</td>
<td>.358770</td>
<td>.359271</td>
<td>.360</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(0)</td>
<td>.312725</td>
<td>.292371</td>
<td>.290080</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.287524</td>
<td>.288363</td>
<td>.288346</td>
<td>.2876</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>.027987</td>
<td>.002442</td>
<td>.001410</td>
<td></td>
</tr>
</tbody>
</table>
Table XIII.C.
Singlet $L = 0$ results at $E = 1.21$

<table>
<thead>
<tr>
<th></th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.160697</td>
<td>0.151366</td>
<td>0.149680</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.149788</td>
<td>0.148868</td>
<td>0.148816</td>
<td>0.1443</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(0)</td>
<td>0.667330</td>
<td>0.563638</td>
<td>0.540766</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.502436</td>
<td>0.504874</td>
<td>0.505086</td>
<td>0.5051</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(+1)</td>
<td>0.150762</td>
<td>0.159443</td>
<td>0.160734</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.160999</td>
<td>0.162050</td>
<td>0.162136</td>
<td>0.16317</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>-0.017572</td>
<td>0.109710</td>
<td>0.129903</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.155812</td>
<td>0.155872</td>
<td>0.155869</td>
<td>0.1545</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>-1.11244</td>
<td>-0.738371</td>
<td>-0.652897</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.521640</td>
<td>-0.520808</td>
<td>-0.520778</td>
<td>-0.5242</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>-0.548436</td>
<td>-0.579998</td>
<td>-0.583443</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.586182</td>
<td>-0.586904</td>
<td>-0.586957</td>
<td>-0.59143</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(0)</td>
<td>0.172651</td>
<td>0.173074</td>
<td>0.173038</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.173080</td>
<td>0.173043</td>
<td>0.173041</td>
<td>0.1722</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.581824</td>
<td>0.586241</td>
<td>0.587501</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.582124</td>
<td>0.588234</td>
<td>0.588750</td>
<td>0.588</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-1)</td>
<td>0.370288</td>
<td>0.361185</td>
<td>0.360402</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.354719</td>
<td>0.358444</td>
<td>0.358752</td>
<td>0.359</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(-1)</td>
<td>0.885421</td>
<td>0.723094</td>
<td>0.695984</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.659742</td>
<td>0.658783</td>
<td>0.658704</td>
<td>0.654</td>
</tr>
</tbody>
</table>

$\alpha$ | 0.011661 | 0.001333 | 0.000487 |
Table XIII.D.
Singlet L = 0 results at E = 1.44.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.270192</td>
<td>0.266359</td>
<td>0.265839</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.265715</td>
<td>0.265710</td>
<td>0.265672</td>
<td>0.2624</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.799038</td>
<td>0.761390</td>
<td>0.752468</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.735025</td>
<td>0.737614</td>
<td>0.737898</td>
<td>0.7389</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.740910</td>
<td>0.801296</td>
<td>0.811663</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.821980</td>
<td>0.825296</td>
<td>0.825638</td>
<td>0.8292</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.692139</td>
<td>-0.514261</td>
<td>-0.477308</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.421339</td>
<td>-0.422045</td>
<td>-0.422187</td>
<td>-0.4261</td>
<td></td>
</tr>
<tr>
<td>$R_{32}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.169343</td>
<td>-0.159340</td>
<td>-0.156637</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.152138</td>
<td>-0.152246</td>
<td>-0.152264</td>
<td>-0.15288</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.263426</td>
<td>-0.287451</td>
<td>-0.291578</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.297108</td>
<td>-0.297406</td>
<td>-0.297434</td>
<td>-0.29887</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.127334</td>
<td>0.127719</td>
<td>0.127711</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.127674</td>
<td>0.127708</td>
<td>0.127710</td>
<td>0.1269</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.377004</td>
<td>0.378663</td>
<td>0.379504</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.377722</td>
<td>0.380260</td>
<td>0.380490</td>
<td>0.380</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.347582</td>
<td>0.344505</td>
<td>0.343979</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.340390</td>
<td>0.342503</td>
<td>0.342710</td>
<td>0.343</td>
<td></td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.214680</td>
<td>0.181423</td>
<td>0.175476</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.167204</td>
<td>0.166980</td>
<td>0.166976</td>
<td>0.1665</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.007695</td>
<td>0.000898</td>
<td>0.000322</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XIII.E.

Singlet L = 0 results at E = 2.25

<table>
<thead>
<tr>
<th>matrix element</th>
<th>RN</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{11} (0)</td>
<td>0.507856</td>
<td>0.507085</td>
<td>0.507149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.507078</td>
<td>0.507122</td>
<td>0.507117</td>
<td>0.1199</td>
<td></td>
</tr>
<tr>
<td>R_{12} (0)</td>
<td>-0.157068</td>
<td>-0.145752</td>
<td>-0.143886</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.140648</td>
<td>-0.140833</td>
<td>-0.140834</td>
<td>1.4076</td>
<td></td>
</tr>
<tr>
<td>R_{13} (0)</td>
<td>-0.233314</td>
<td>-0.238003</td>
<td>-0.239192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.240369</td>
<td>-0.240850</td>
<td>-0.240856</td>
<td>0.7505</td>
<td></td>
</tr>
<tr>
<td>R_{22} (+1)</td>
<td>0.260403</td>
<td>0.253041</td>
<td>0.251526</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.249291</td>
<td>0.249235</td>
<td>0.249227</td>
<td>-0.37442</td>
<td></td>
</tr>
<tr>
<td>R_{23} (0)</td>
<td>0.840909</td>
<td>0.903756</td>
<td>0.915951</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.934003</td>
<td>0.934032</td>
<td>0.933942</td>
<td>-3.0550</td>
<td></td>
</tr>
<tr>
<td>R_{33} (+1)</td>
<td>0.092204</td>
<td>0.098810</td>
<td>0.100239</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.102504</td>
<td>0.102483</td>
<td>0.102474</td>
<td>-0.15274</td>
<td></td>
</tr>
<tr>
<td>Q_{11} (-1)</td>
<td>0.804825</td>
<td>0.803938</td>
<td>0.804080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.804030</td>
<td>0.804036</td>
<td>0.804042</td>
<td>0.836</td>
<td></td>
</tr>
<tr>
<td>Q_{12} (-3)</td>
<td>0.734625</td>
<td>0.711439</td>
<td>0.712129</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-3)</td>
<td>0.710621</td>
<td>0.713149</td>
<td>0.713191</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>Q_{13} (-2)</td>
<td>0.754580</td>
<td>0.752232</td>
<td>0.752441</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.748838</td>
<td>0.752041</td>
<td>0.752153</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>Q_{22} (0)</td>
<td>0.498734</td>
<td>0.480420</td>
<td>0.476615</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.470884</td>
<td>0.470848</td>
<td>0.470856</td>
<td>0.3137</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>0.005382</td>
<td>0.000433</td>
<td>0.000145</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XIII.F.

Singlet $L = 0$ results at $E = 4.00$

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>4SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.849177</td>
<td>0.849681</td>
<td>0.849374</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6)</td>
<td>0.850135</td>
<td>0.849382</td>
<td>0.849376</td>
<td>0.8383</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(+1)</td>
<td>-0.120968</td>
<td>-0.119304</td>
<td>-0.118908</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.118340</td>
<td>-0.118404</td>
<td>-0.118407</td>
<td>-0.11673</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.544700</td>
<td>-0.575827</td>
<td>-0.582097</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.590054</td>
<td>-0.591871</td>
<td>-0.591865</td>
<td>-0.5836</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(+1)</td>
<td>0.578295</td>
<td>0.566487</td>
<td>0.564163</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.560190</td>
<td>0.560814</td>
<td>0.560796</td>
<td>0.55326</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(+1)</td>
<td>0.184027</td>
<td>0.194697</td>
<td>0.196956</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.199933</td>
<td>0.200393</td>
<td>0.200371</td>
<td>0.19726</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>0.133861</td>
<td>0.143288</td>
<td>0.145408</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.148390</td>
<td>0.148692</td>
<td>0.148678</td>
<td>0.14729</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.588864</td>
<td>0.589318</td>
<td>0.589253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.590123</td>
<td>0.589273</td>
<td>0.589272</td>
<td>0.579</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-2)</td>
<td>0.518552</td>
<td>0.501558</td>
<td>0.497349</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.492822</td>
<td>0.491439</td>
<td>0.491510</td>
<td>0.49</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-2)</td>
<td>0.323452</td>
<td>0.343998</td>
<td>0.347838</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.350133</td>
<td>0.353623</td>
<td>0.353687</td>
<td>0.35</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(0)</td>
<td>0.249174</td>
<td>0.244149</td>
<td>0.243085</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.241426</td>
<td>0.241456</td>
<td>0.241462</td>
<td>0.2412</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.002090</td>
<td>0.000189</td>
<td>0.000071</td>
<td></td>
</tr>
</tbody>
</table>
Table XIV.

Triplet $L = 0$, three channel results, calculated in the 1s-2s-2p approximation by integration scheme v. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BSS" column contains values from Reference 5.
Table XIV.A.

Triplet $L = 0$ results at $F = 0.81$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_{N}$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (+2)</td>
<td>0.169489</td>
<td>0.169295</td>
<td>0.169339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+2)</td>
<td>.169341</td>
<td>.169326</td>
<td>.169330</td>
<td>0.16655</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-.235685</td>
<td>-.342909</td>
<td>-.359996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.364518</td>
<td>-.382763</td>
<td>-.384146</td>
<td>-.3650</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>.490962</td>
<td>.428434</td>
<td>.420885</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.388491</td>
<td>.393560</td>
<td>.394778</td>
<td>.3940</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td>-.493670</td>
<td>-.664376</td>
<td>-.678109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.678037</td>
<td>-.684476</td>
<td>-.684652</td>
<td>-.6858</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (0)</td>
<td>.606595</td>
<td>.204940</td>
<td>.117956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>1.07544</td>
<td>-.988583</td>
<td>-1.03193</td>
<td>-.94</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$ (+1)</td>
<td>.130999</td>
<td>.138886</td>
<td>.139808</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.142618</td>
<td>.140336</td>
<td>.140275</td>
<td>.14022</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (+1)</td>
<td>.368718</td>
<td>.368693</td>
<td>.368688</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.368696</td>
<td>.368690</td>
<td>.368690</td>
<td>.36866</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (-2)</td>
<td>.115170</td>
<td>.127885</td>
<td>.128251</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>.118506</td>
<td>.127136</td>
<td>.127976</td>
<td>.12</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$ (-3)</td>
<td>.682448</td>
<td>.673575</td>
<td>.695723</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-3)</td>
<td>.634346</td>
<td>.677187</td>
<td>.682026</td>
<td>.7</td>
<td></td>
</tr>
<tr>
<td>$Q_{22}$ (+2)</td>
<td>.136303</td>
<td>.158761</td>
<td>.161020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+2)</td>
<td>.159997</td>
<td>.162163</td>
<td>.162223</td>
<td>.16236</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>.111738</td>
<td>.011326</td>
<td>.003704</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XIV.B.

Triplet $L = 0$ results at $E = 1.00$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>E/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (+1)</td>
<td>0.720970</td>
<td>0.718710</td>
<td>0.718826</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.721022</td>
<td>0.719382</td>
<td>0.719267</td>
<td>0.72054</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (+1)</td>
<td>0.402892</td>
<td>0.415785</td>
<td>0.422198</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.433596</td>
<td>0.430715</td>
<td>0.430722</td>
<td>0.45532</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$ (+1)</td>
<td>-0.310765</td>
<td>-0.258374</td>
<td>-0.251035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.241538</td>
<td>-0.238974</td>
<td>-0.238988</td>
<td>-0.25610</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (+2)</td>
<td>0.131619</td>
<td>0.144180</td>
<td>0.148925</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+2)</td>
<td>0.157380</td>
<td>0.155171</td>
<td>0.155062</td>
<td>0.16781</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>-1.10059</td>
<td>-0.981300</td>
<td>-0.970816</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.961610</td>
<td>-0.945908</td>
<td>-0.945306</td>
<td>-1.0317</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$ (+1)</td>
<td>0.906384</td>
<td>0.654365</td>
<td>0.619645</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.574865</td>
<td>0.563857</td>
<td>0.563522</td>
<td>0.6219</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (+1)</td>
<td>0.290714</td>
<td>0.290663</td>
<td>0.290670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.290665</td>
<td>0.290669</td>
<td>0.290670</td>
<td>0.29062</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (+2)</td>
<td>0.340874</td>
<td>0.366385</td>
<td>0.367331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.365138</td>
<td>0.371049</td>
<td>0.371516</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$ (+2)</td>
<td>0.339234</td>
<td>0.340676</td>
<td>0.336725</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.326458</td>
<td>0.331587</td>
<td>0.331896</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.412278</td>
<td>0.555035</td>
<td>0.585003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.629298</td>
<td>0.630954</td>
<td>0.630917</td>
<td>0.62512</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha$ | 0.017818 | 0.002607 | 0.000862 |
Table XIV.C.

Triplet L = 0 results at E = 1.21.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>4%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (+1)</td>
<td>0.390077</td>
<td>0.389961</td>
<td>0.389990</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.389969</td>
<td>0.389986</td>
<td>0.389988</td>
<td>0.38892</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>0.521588</td>
<td>0.533712</td>
<td>0.537802</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.538330</td>
<td>0.541798</td>
<td>0.542022</td>
<td>0.5389</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>0.253200</td>
<td>0.214433</td>
<td>0.207176</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.193248</td>
<td>0.195011</td>
<td>0.195075</td>
<td>0.1942</td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>0.074254</td>
<td>0.094690</td>
<td>0.099015</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.105671</td>
<td>0.105688</td>
<td>0.105691</td>
<td>0.10557</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>0.149865</td>
<td>0.150064</td>
<td>0.149827</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.149191</td>
<td>0.149201</td>
<td>0.149210</td>
<td>0.14925</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>1.04112</td>
<td>0.811310</td>
<td>0.766866</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.700818</td>
<td>0.700624</td>
<td>0.700851</td>
<td>0.7018</td>
</tr>
<tr>
<td>$Q_{11}$ (+1)</td>
<td>0.229763</td>
<td>0.229795</td>
<td>0.229787</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.229794</td>
<td>0.229788</td>
<td>0.229788</td>
<td>0.22973</td>
</tr>
<tr>
<td>$Q_{12}$ (-2)</td>
<td>0.506152</td>
<td>0.505687</td>
<td>0.509565</td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.506063</td>
<td>0.512415</td>
<td>0.512824</td>
<td>0.51</td>
</tr>
<tr>
<td>$Q_{13}$ (-2)</td>
<td>0.705589</td>
<td>0.686389</td>
<td>0.686250</td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.673272</td>
<td>0.681326</td>
<td>0.681924</td>
<td>0.68</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.189721</td>
<td>0.215311</td>
<td>0.221100</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.230174</td>
<td>0.230173</td>
<td>0.230156</td>
<td>0.23015</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.014049</td>
<td>0.001301</td>
<td>0.000502</td>
<td></td>
</tr>
</tbody>
</table>
Table XIV. D.

Triplet L = 0 results at E = 1.44.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (+1)</td>
<td>0.286553</td>
<td>0.286506</td>
<td>0.286516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.286520</td>
<td>0.286515</td>
<td>0.286516</td>
<td>0.28588</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>0.422175</td>
<td>0.425727</td>
<td>0.427477</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.427770</td>
<td>0.42954</td>
<td>0.429063</td>
<td>0.4270</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$ (-1)</td>
<td>-1.31150</td>
<td>-1.00648</td>
<td>-0.956053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>-0.878819</td>
<td>-0.879944</td>
<td>-0.880114</td>
<td>-0.879</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (-1)</td>
<td>-1.46130</td>
<td>0.023438</td>
<td>0.285666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.765320</td>
<td>0.760373</td>
<td>0.759584</td>
<td>0.746</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>-0.127955</td>
<td>-0.131468</td>
<td>-0.131986</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>-0.132624</td>
<td>-0.132628</td>
<td>-0.132629</td>
<td>-0.13268</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>0.621567</td>
<td>0.459640</td>
<td>0.427389</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.379654</td>
<td>0.379320</td>
<td>0.379410</td>
<td>0.3798</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (+1)</td>
<td>0.182672</td>
<td>0.182737</td>
<td>0.182731</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.182724</td>
<td>0.182730</td>
<td>0.182730</td>
<td>0.18266</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (-2)</td>
<td>0.551921</td>
<td>0.546492</td>
<td>0.548388</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.545730</td>
<td>0.548855</td>
<td>0.549126</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$ (-2)</td>
<td>0.973282</td>
<td>0.954745</td>
<td>0.956788</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.949406</td>
<td>0.954990</td>
<td>0.955474</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.173413</td>
<td>0.171856</td>
<td>0.171770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.171785</td>
<td>0.171792</td>
<td>0.171794</td>
<td>0.17193</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha$        | 0.009903| 0.000879| 0.000332|         |         |
Table XIV.E.
Triplet $L = 0$ results at $E = 2.25$.

<table>
<thead>
<tr>
<th>matrix element $R_{N}$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (+1)</td>
<td>0.171171</td>
<td>0.171189</td>
<td>0.171179</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.171195</td>
<td>.171178</td>
<td>.171178</td>
<td>.16284</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>.912830</td>
<td>.904400</td>
<td>.902917</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.898052</td>
<td>.899852</td>
<td>.899991</td>
<td>.5997</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>.190343</td>
<td>.225636</td>
<td>.233355</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.243945</td>
<td>.244269</td>
<td>.244299</td>
<td>.1035</td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>-.147868</td>
<td>-.137464</td>
<td>-.135213</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.131626</td>
<td>-.131694</td>
<td>-.131706</td>
<td>-.24569</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>-.135886</td>
<td>-.142863</td>
<td>-.144114</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.145931</td>
<td>-.145944</td>
<td>-.145942</td>
<td>-.19941</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>.305794</td>
<td>.188744</td>
<td>.165106</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.129184</td>
<td>.129437</td>
<td>.129437</td>
<td>-.1209</td>
</tr>
<tr>
<td>$Q_{11}$ (0)</td>
<td>.994725</td>
<td>.994648</td>
<td>.994689</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.994723</td>
<td>.994677</td>
<td>.994681</td>
<td>.9657</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td>.231565</td>
<td>.218436</td>
<td>.216280</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.211901</td>
<td>.212652</td>
<td>.212718</td>
<td>.045</td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td>.197184</td>
<td>.208961</td>
<td>.211181</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.213788</td>
<td>.214618</td>
<td>.214657</td>
<td>.106</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>.129544</td>
<td>.124688</td>
<td>.123704</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.122195</td>
<td>.122223</td>
<td>.122228</td>
<td>.13909</td>
</tr>
</tbody>
</table>

$\alpha$ = .003607 .000442 .000151
Table XIV.F.

Triplet $L = 0$ results at $E = 4.00$.\(^a\)

<table>
<thead>
<tr>
<th>matrix element</th>
<th>R(_N)</th>
<th>40</th>
<th>80</th>
<th>100</th>
<th>ESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(_{11}) (+1)</td>
<td>0.122904</td>
<td>0.123004</td>
<td>0.122925</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.122984</td>
<td>0.122948</td>
<td>0.122947</td>
<td>0.12202</td>
<td></td>
</tr>
<tr>
<td>R(_{12}) (0)</td>
<td>-0.946327</td>
<td>-0.937914</td>
<td>-0.933223</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.925218</td>
<td>-0.925688</td>
<td>-0.925627</td>
<td>-0.9043</td>
<td></td>
</tr>
<tr>
<td>R(_{13}) (0)</td>
<td>-0.442499</td>
<td>-0.461502</td>
<td>-0.463400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.476553</td>
<td>-0.479066</td>
<td>-0.479012</td>
<td>-0.4699</td>
<td></td>
</tr>
<tr>
<td>R(_{22}) (+1)</td>
<td>0.753560</td>
<td>0.742579</td>
<td>0.739845</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.730988</td>
<td>0.731754</td>
<td>0.731672</td>
<td>0.72115</td>
<td></td>
</tr>
<tr>
<td>R(_{23}) (+1)</td>
<td>0.222697</td>
<td>0.233497</td>
<td>0.235498</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.244384</td>
<td>0.244863</td>
<td>0.244784</td>
<td>0.24055</td>
<td></td>
</tr>
<tr>
<td>R(_{33}) (+1)</td>
<td>0.153703</td>
<td>0.162141</td>
<td>0.163865</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.171474</td>
<td>0.171761</td>
<td>0.171717</td>
<td>0.17000</td>
<td></td>
</tr>
<tr>
<td>Q(_{11}) (0)</td>
<td>0.399505</td>
<td>0.399582</td>
<td>0.399634</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.399903</td>
<td>0.399631</td>
<td>0.399629</td>
<td>0.3979</td>
<td></td>
</tr>
<tr>
<td>Q(_{12}) (-2)</td>
<td>0.327025</td>
<td>0.317621</td>
<td>0.314568</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.307001</td>
<td>0.305305</td>
<td>0.305357</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Q(_{13}) (-2)</td>
<td>0.498768</td>
<td>0.514537</td>
<td>0.511922</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.511271</td>
<td>0.522652</td>
<td>0.522841</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Q(_{22}) (0)</td>
<td>0.811121</td>
<td>0.800658</td>
<td>0.798448</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.789233</td>
<td>0.789291</td>
<td>0.789333</td>
<td>0.7894</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.002155</td>
<td>0.000411</td>
<td>0.000309</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Note: $R_N$ values are different.
Table XV.

Convergence with respect to increasing \( R_N \) of projected results from representative three channel \((L = 0)\) calculations in the \(1s-2s-2p\) approximation. Entries are the fractional changes in each projected matrix element as integration is extended over the range indicated. Singlet and triplet states are indicated with "s" and "t".

<table>
<thead>
<tr>
<th>( E )</th>
<th>fractional changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 - 80</td>
</tr>
<tr>
<td>1.00 s</td>
<td></td>
</tr>
<tr>
<td>R_{11}</td>
<td>-0.00132</td>
</tr>
<tr>
<td>R_{12}</td>
<td>0.032046</td>
</tr>
<tr>
<td>R_{13}</td>
<td>-0.007229</td>
</tr>
<tr>
<td>R_{22}</td>
<td>-0.023390</td>
</tr>
<tr>
<td>R_{23}</td>
<td>0.000232</td>
</tr>
<tr>
<td>R_{33}</td>
<td>-0.000098</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>-0.00151</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>-0.015956</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>-0.014041</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>-0.028885</td>
</tr>
<tr>
<td>t</td>
<td></td>
</tr>
<tr>
<td>R_{11}</td>
<td>0.002558</td>
</tr>
<tr>
<td>R_{12}</td>
<td>0.010200</td>
</tr>
<tr>
<td>R_{13}</td>
<td>-0.014431</td>
</tr>
<tr>
<td>R_{22}</td>
<td>0.016246</td>
</tr>
<tr>
<td>R_{23}</td>
<td>-0.01638</td>
</tr>
<tr>
<td>R_{33}</td>
<td>0.021655</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>-0.000014</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>-0.002358</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>-0.011820</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>-0.002661</td>
</tr>
<tr>
<td>2.25 s</td>
<td></td>
</tr>
<tr>
<td>R_{11}</td>
<td>-0.000081</td>
</tr>
<tr>
<td>R_{12}</td>
<td>0.000753</td>
</tr>
<tr>
<td>R_{13}</td>
<td>0.001578</td>
</tr>
<tr>
<td>R_{22}</td>
<td>0.000373</td>
</tr>
<tr>
<td>R_{23}</td>
<td>0.000123</td>
</tr>
<tr>
<td>R_{33}</td>
<td>0.000273</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>-0.000040</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>-0.002816</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>-0.003538</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>0.000127</td>
</tr>
</tbody>
</table>
Table XV. (cont.)

<table>
<thead>
<tr>
<th>E</th>
<th>fractional changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 - 80</td>
</tr>
<tr>
<td>2.25 t</td>
<td>R_{11}</td>
</tr>
<tr>
<td></td>
<td>R_{12}</td>
</tr>
<tr>
<td></td>
<td>R_{13}</td>
</tr>
<tr>
<td></td>
<td>R_{22}</td>
</tr>
<tr>
<td></td>
<td>R_{23}</td>
</tr>
<tr>
<td></td>
<td>R_{33}</td>
</tr>
<tr>
<td></td>
<td>Q_{11}</td>
</tr>
<tr>
<td></td>
<td>Q_{12}</td>
</tr>
<tr>
<td></td>
<td>Q_{13}</td>
</tr>
<tr>
<td></td>
<td>Q_{22}</td>
</tr>
</tbody>
</table>
Table XVI.
Results of calculations on the singlet \( L = 0 \) state at \( E = 2.25 \), showing dependence on step size. The integration schemes are given in the text. For each matrix element, the first row entries are the results at \( R_N = 30 \), while second row entries are the results at \( R_N = 40 \).

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>i.</th>
<th>ii.</th>
<th>iii.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} ) (0)</td>
<td></td>
<td>0.482227</td>
<td>0.430550</td>
<td>0.111506</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>.504975</td>
<td>.508389</td>
<td>.517763</td>
</tr>
<tr>
<td>( R_{12} ) (0)</td>
<td></td>
<td>-.117061</td>
<td>-.054917</td>
<td>1.79787</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>-.154204</td>
<td>.158142</td>
<td>-.176850</td>
</tr>
<tr>
<td>( R_{13} ) (0)</td>
<td></td>
<td>-.209224</td>
<td>-.185838</td>
<td>.826146</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>-.231433</td>
<td>-.234072</td>
<td>-.244588</td>
</tr>
<tr>
<td>( R_{22} ) (+1)</td>
<td></td>
<td>.269370</td>
<td>.327541</td>
<td>-1.09530</td>
</tr>
<tr>
<td>(+1)</td>
<td></td>
<td>.260177</td>
<td>.260395</td>
<td>.260534</td>
</tr>
<tr>
<td>( R_{23} ) (0)</td>
<td></td>
<td>.849283</td>
<td>.120554</td>
<td>-6.70776</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>.839555</td>
<td>.840585</td>
<td>.841260</td>
</tr>
<tr>
<td>( R_{33} ) (0)</td>
<td></td>
<td>.923025</td>
<td>1.13776</td>
<td>-3.26765</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>.921089</td>
<td>.921476</td>
<td>.921778</td>
</tr>
<tr>
<td>( Q_{11} ) (-1)</td>
<td></td>
<td>.757742</td>
<td>.641152</td>
<td>.470971</td>
</tr>
<tr>
<td>(-1)</td>
<td></td>
<td>.798773</td>
<td>.805514</td>
<td>.819628</td>
</tr>
<tr>
<td>( Q_{12} ) (-3)</td>
<td></td>
<td>.480954</td>
<td>.507638</td>
<td>3.99514</td>
</tr>
<tr>
<td>(-3)</td>
<td></td>
<td>.716138</td>
<td>.742788</td>
<td>.883278</td>
</tr>
<tr>
<td>( Q_{13} ) (-2)</td>
<td></td>
<td>.672002</td>
<td>.573343</td>
<td>1.16485</td>
</tr>
<tr>
<td>(-2)</td>
<td></td>
<td>.748213</td>
<td>.758350</td>
<td>.796243</td>
</tr>
<tr>
<td>( Q_{22} ) (0)</td>
<td></td>
<td>.506876</td>
<td>.503496</td>
<td>.450141</td>
</tr>
<tr>
<td>(0)</td>
<td></td>
<td>.498746</td>
<td>.498757</td>
<td>.498522</td>
</tr>
</tbody>
</table>
Table XVII.
Results of calculations on singlet $L = 1$ state at $E = 1.00$ in
the $1s-2s-2p$ exchange approximation showing dependence on step
size. Integration schemes i.-iii. are given in the text. For
each matrix element, the number in parentheses gives the power
of ten by which the entries in that row should be multiplied.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>scheme</th>
<th>i.</th>
<th>ii.</th>
<th>iii.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (-1)</td>
<td></td>
<td>-0.124352</td>
<td>-0.124531</td>
<td>-0.124576</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td></td>
<td>-0.246565</td>
<td>-0.246477</td>
<td>-0.246455</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td></td>
<td>-0.172266</td>
<td>-0.172167</td>
<td>-0.172142</td>
</tr>
<tr>
<td>$R_{14}$ (0)</td>
<td></td>
<td>-0.525649</td>
<td>-0.525492</td>
<td>-0.525453</td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td></td>
<td>0.920267</td>
<td>0.920032</td>
<td>0.919973</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td></td>
<td>0.132635</td>
<td>0.132612</td>
<td>0.132606</td>
</tr>
<tr>
<td>$R_{24}$ (+1)</td>
<td></td>
<td>0.132793</td>
<td>0.132751</td>
<td>0.132741</td>
</tr>
<tr>
<td>$R_{33}$ (+1)</td>
<td></td>
<td>0.113270</td>
<td>0.113234</td>
<td>0.113224</td>
</tr>
<tr>
<td>$R_{34}$ (+1)</td>
<td></td>
<td>0.204651</td>
<td>0.204612</td>
<td>0.204602</td>
</tr>
<tr>
<td>$R_{44}$ (0)</td>
<td></td>
<td>0.289208</td>
<td>0.288372</td>
<td>0.288163</td>
</tr>
<tr>
<td>$Q_{11}$ (-2)</td>
<td></td>
<td>0.996424</td>
<td>0.995831</td>
<td>0.995683</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td></td>
<td>0.190280</td>
<td>0.190218</td>
<td>0.190203</td>
</tr>
<tr>
<td>$Q_{13}$ (0)</td>
<td></td>
<td>0.105604</td>
<td>0.105572</td>
<td>0.105564</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td></td>
<td>0.111275</td>
<td>0.111284</td>
<td>0.111286</td>
</tr>
</tbody>
</table>
Table XVIII.

Analysis of step size dependence of the results in Table XVII. The first two columns give the changes in matrix elements $M$ calculated with step sizes $\Delta_\alpha = 0.05$, $\Delta_\beta = 0.025$, and $\Delta_\gamma = 0.0125$. The results of extrapolation to zero step size and the corresponding Quadratic Rule coefficients are shown. Also, the error due to finite step size $\Delta_\beta$ is evaluated. The numbers in parentheses give the power of ten by which the matrix element differences and $M(0)$ should be multiplied.

<table>
<thead>
<tr>
<th>matrix element $M$</th>
<th>$M(\Delta_\alpha) - M(\Delta_\beta)$</th>
<th>$M(\Delta_\beta) - M(\Delta_\gamma)$</th>
<th>$M(0)^a$</th>
<th>$q^b$</th>
<th>$f(\Delta_\beta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (-1)</td>
<td>0.000179</td>
<td>0.000045</td>
<td>-0.124591</td>
<td>0.96</td>
<td>(-2) -0.000482</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-0.000088</td>
<td>-0.00022</td>
<td>-0.246448</td>
<td>-0.467</td>
<td>(-1) 0.000119</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>-0.000099</td>
<td>-0.00025</td>
<td>-0.172134</td>
<td>-0.533</td>
<td>(-1) 0.000194</td>
</tr>
<tr>
<td>$R_{14}$ (0)</td>
<td>-0.000157</td>
<td>-0.00039</td>
<td>-0.525440</td>
<td>-0.832</td>
<td>(-1) 0.000099</td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td>0.000235</td>
<td>0.00059</td>
<td>0.919953</td>
<td>0.126</td>
<td>(0) 0.000086</td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>0.000023</td>
<td>0.00006</td>
<td>0.132604</td>
<td>0.128</td>
<td>(0) 0.000060</td>
</tr>
<tr>
<td>$R_{24}$ (+1)</td>
<td>0.000042</td>
<td>0.00010</td>
<td>0.132738</td>
<td>0.213</td>
<td>(0) 0.000100</td>
</tr>
<tr>
<td>$R_{33}$ (+1)</td>
<td>0.000036</td>
<td>0.00010</td>
<td>0.113221</td>
<td>0.213</td>
<td>(0) 0.000118</td>
</tr>
<tr>
<td>$R_{34}$ (+1)</td>
<td>0.000039</td>
<td>0.00010</td>
<td>0.204599</td>
<td>0.213</td>
<td>(0) 0.000065</td>
</tr>
<tr>
<td>$R_{44}$ (0)</td>
<td>0.000836</td>
<td>0.000209</td>
<td>0.288093</td>
<td>0.446</td>
<td>(0) 0.000967</td>
</tr>
<tr>
<td>$Q_{11}$ (-2)</td>
<td>0.00593</td>
<td>0.00148</td>
<td>0.995634</td>
<td>0.316</td>
<td>(-2) 0.000198</td>
</tr>
<tr>
<td>$Q_{12}$ (-1)</td>
<td>0.00062</td>
<td>0.00015</td>
<td>0.190198</td>
<td>0.320</td>
<td>(-2) 0.000105</td>
</tr>
<tr>
<td>$Q_{13}$ (0)</td>
<td>0.00032</td>
<td>0.00008</td>
<td>0.105561</td>
<td>0.171</td>
<td>(-1) 0.000101</td>
</tr>
<tr>
<td>$Q_{22}$ (+1)</td>
<td>0.000009</td>
<td>0.00002</td>
<td>0.11287</td>
<td>-0.427</td>
<td>(-1) 0.000024</td>
</tr>
</tbody>
</table>

$^a$ Value extrapolated to zero step size by Eq. (1.42) of text.

$^b$ Numbers in parentheses give the power of ten by which the preceding number should be multiplied.
Table XIX.

Singlet $L = 1$, four channel results, calculated in the $1s-2s-2p$ approximation by integration scheme $v$. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BSS" column contains values from Reference 5.
Table XIX.A.

Singlet L = 1 results at E = 0.81.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>R_N</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{11}</td>
<td>(-1)</td>
<td>-0.552125</td>
<td>-0.552864</td>
<td>0.552696</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.552810</td>
<td>-0.552617</td>
<td>-0.552608</td>
<td>-0.560</td>
</tr>
<tr>
<td>R_{12}</td>
<td>(-2)</td>
<td>0.309574</td>
<td>-0.301582</td>
<td>-0.464967</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>-0.641040</td>
<td>-0.723270</td>
<td>-0.728062</td>
<td>-0.70</td>
</tr>
<tr>
<td>R_{13}</td>
<td>(0)</td>
<td>0.158161</td>
<td>0.158530</td>
<td>0.158580</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.156831</td>
<td>0.158136</td>
<td>0.158242</td>
<td>0.1596</td>
</tr>
<tr>
<td>R_{14}</td>
<td>(-1)</td>
<td>-0.603191</td>
<td>-0.582913</td>
<td>-0.580683</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.603904</td>
<td>-0.586086</td>
<td>-0.584636</td>
<td>-0.591</td>
</tr>
<tr>
<td>R_{22}</td>
<td>(0)</td>
<td>0.702101</td>
<td>0.684640</td>
<td>0.660811</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.624710</td>
<td>0.611034</td>
<td>0.610460</td>
<td>0.6131</td>
</tr>
<tr>
<td>R_{23}</td>
<td>(-2)</td>
<td>-4.31377</td>
<td>-14.6191</td>
<td>-8.60246</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>-2.44322</td>
<td>0.047991</td>
<td>0.185092</td>
<td>0.20</td>
</tr>
<tr>
<td>R_{24}</td>
<td>(0)</td>
<td>0.040761</td>
<td>0.391531</td>
<td>0.465588</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.567084</td>
<td>0.574690</td>
<td>0.574601</td>
<td>0.5759</td>
</tr>
<tr>
<td>R_{33}</td>
<td>(0)</td>
<td>-0.761491</td>
<td>-0.851342</td>
<td>-0.858752</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.855709</td>
<td>-0.862099</td>
<td>-0.862442</td>
<td>-0.8728</td>
</tr>
<tr>
<td>R_{44}</td>
<td>(0)</td>
<td>-0.624932</td>
<td>-0.684829</td>
<td>-0.680515</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.647802</td>
<td>-0.663891</td>
<td>-0.664867</td>
<td>-0.6716</td>
</tr>
<tr>
<td>R_{44}</td>
<td>(+1)</td>
<td>-1.15255</td>
<td>-1.10652</td>
<td>-1.07730</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-1.01722</td>
<td>-1.02494</td>
<td>-1.02538</td>
<td>-1.0264</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>(-2)</td>
<td>0.955200</td>
<td>0.960806</td>
<td>0.959944</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.961188</td>
<td>0.959999</td>
<td>0.960003</td>
<td>0.98</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>(-2)</td>
<td>0.702426</td>
<td>0.523384</td>
<td>0.489429</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.414197</td>
<td>0.438248</td>
<td>0.440940</td>
<td>0.45</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>(-1)</td>
<td>0.716181</td>
<td>0.736645</td>
<td>0.739945</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.739316</td>
<td>0.744198</td>
<td>0.744473</td>
<td>0.754</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>(+2)</td>
<td>0.159466</td>
<td>0.153652</td>
<td>0.151081</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.148287</td>
<td>0.146449</td>
<td>0.146358</td>
<td>0.14697</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td>0.338806</td>
<td>0.010596</td>
<td>0.004931</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) These values do not include R_{22}, for which \( a = 0.646037, 0.530600, \) and 0.528969.
Table XIX.B.

Singlet \( L = 1 \) results at \( E = 1.00 \)

<table>
<thead>
<tr>
<th>matrix element ( R_N )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} ) (-1)</td>
<td>-0.122231</td>
<td>-0.151289</td>
<td>-0.153447</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>-0.151822</td>
<td>-0.154842</td>
<td>-0.155036</td>
<td>-0.160</td>
</tr>
<tr>
<td>( R_{12} ) (0)</td>
<td>-0.247125</td>
<td>-0.184321</td>
<td>-0.173274</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.156181</td>
<td>-0.156461</td>
<td>-0.156587</td>
<td>-0.1564</td>
</tr>
<tr>
<td>( R_{13} ) (0)</td>
<td>-0.173652</td>
<td>-0.171065</td>
<td>-0.172150</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.172246</td>
<td>-0.174051</td>
<td>-0.174247</td>
<td>-0.1742</td>
</tr>
<tr>
<td>( R_{14} ) (0)</td>
<td>-0.527162</td>
<td>-0.534183</td>
<td>-0.536542</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.535641</td>
<td>-0.539430</td>
<td>-0.539755</td>
<td>-0.5403</td>
</tr>
<tr>
<td>( R_{22} ) (0)</td>
<td>0.921529</td>
<td>0.545301</td>
<td>0.481881</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.395177</td>
<td>0.389009</td>
<td>0.389151</td>
<td>0.3901</td>
</tr>
<tr>
<td>( R_{23} ) (0)</td>
<td>1.32949</td>
<td>1.08648</td>
<td>1.04178</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.979459</td>
<td>0.971947</td>
<td>0.971963</td>
<td>0.9745</td>
</tr>
<tr>
<td>( R_{24} ) (+1)</td>
<td>0.133119</td>
<td>0.120475</td>
<td>0.117877</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.113810</td>
<td>0.113602</td>
<td>0.113621</td>
<td>0.11385</td>
</tr>
<tr>
<td>( R_{33} ) (+1)</td>
<td>0.113983</td>
<td>0.120001</td>
<td>0.122127</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.125856</td>
<td>0.125369</td>
<td>0.125364</td>
<td>0.12562</td>
</tr>
<tr>
<td>( R_{44} ) (+1)</td>
<td>0.205418</td>
<td>0.216828</td>
<td>0.219727</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>0.223007</td>
<td>0.223883</td>
<td>0.225969</td>
<td>0.22451</td>
</tr>
<tr>
<td>( R_{44} ) (0)</td>
<td>0.297134</td>
<td>0.481181</td>
<td>0.520407</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.577547</td>
<td>0.576652</td>
<td>0.576655</td>
<td>0.5796</td>
</tr>
<tr>
<td>( Q_{11} ) (-1)</td>
<td>0.099879</td>
<td>0.100148</td>
<td>0.100062</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.100249</td>
<td>0.100098</td>
<td>0.100093</td>
<td>0.101</td>
</tr>
<tr>
<td>( Q_{12} ) (-1)</td>
<td>0.189948</td>
<td>0.159862</td>
<td>0.153600</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.142204</td>
<td>0.144464</td>
<td>0.144681</td>
<td>0.145</td>
</tr>
<tr>
<td>( Q_{13} ) (0)</td>
<td>0.105738</td>
<td>0.109138</td>
<td>0.109690</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.110032</td>
<td>0.110524</td>
<td>0.110554</td>
<td>0.1105</td>
</tr>
<tr>
<td>( Q_{22} ) (0)</td>
<td>1.10625</td>
<td>0.788489</td>
<td>0.744674</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.690773</td>
<td>0.691611</td>
<td>0.691697</td>
<td>0.6943</td>
</tr>
</tbody>
</table>

\( \alpha = 0.041394 \) \( , \ 0.004487 \) \( , \ 0.001607 \)
<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(-1)</td>
<td>-.325450</td>
<td>-.346779</td>
<td>-.347284</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.347734</td>
<td>.347779</td>
<td>.347626</td>
<td>-.352</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(0)</td>
<td>.271830</td>
<td>.237035</td>
<td>.230981</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.220573</td>
<td>.221821</td>
<td>.221974</td>
<td>.2222</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(-2)</td>
<td>1.16676</td>
<td>.591288</td>
<td>.402767</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>.268062</td>
<td>.144559</td>
<td>.132268</td>
<td>.16</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(0)</td>
<td>-.476371</td>
<td>-.487038</td>
<td>-.489838</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.491591</td>
<td>-.493554</td>
<td>-.493716</td>
<td>-.4943</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>.844564</td>
<td>.642435</td>
<td>.604808</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.549369</td>
<td>.549411</td>
<td>.549605</td>
<td>.5497</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>.991750</td>
<td>.943940</td>
<td>.934241</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.920449</td>
<td>.919280</td>
<td>.919275</td>
<td>.9197</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>.877332</td>
<td>.872022</td>
<td>.869680</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.865585</td>
<td>.864766</td>
<td>.864902</td>
<td>.8650</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(0)</td>
<td>-.441647</td>
<td>-.371906</td>
<td>-.356624</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.333549</td>
<td>-.333318</td>
<td>-.333282</td>
<td>-.3344</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(+1)</td>
<td>.135465</td>
<td>.145340</td>
<td>.145224</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.147654</td>
<td>.147927</td>
<td>.147949</td>
<td>.14811</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>.132954</td>
<td>.132404</td>
<td>.132560</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.132399</td>
<td>.132537</td>
<td>.132536</td>
<td>.133</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>.302494</td>
<td>.263234</td>
<td>.256514</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.243155</td>
<td>.245743</td>
<td>.245982</td>
<td>.246</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>.105207</td>
<td>.108645</td>
<td>.109406</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.109938</td>
<td>.110386</td>
<td>.110421</td>
<td>.1105</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(+1)</td>
<td>.140891</td>
<td>.115052</td>
<td>.110743</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.104840</td>
<td>.104846</td>
<td>.104852</td>
<td>.10493</td>
</tr>
</tbody>
</table>

$\alpha^a = 0.012499, 0.001406, 0.000496$

$^a$ These values do not include $R_{12}$, for which $\alpha = 21.4057, 0.274377$, and 0.093305.
Table XIX.D.

Singlet L = 1 results at E = 1.44

<table>
<thead>
<tr>
<th>matrix element</th>
<th>RN 40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{11}</td>
<td>-0.150682</td>
<td>-0.152722</td>
<td>-0.152914</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.153902</td>
<td>-0.153623</td>
<td>-0.153515</td>
<td>-0.160</td>
</tr>
<tr>
<td>R_{12}</td>
<td>-0.349221</td>
<td>-0.330220</td>
<td>-0.326527</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.319413</td>
<td>-0.320768</td>
<td>-0.320902</td>
<td>-0.326</td>
</tr>
<tr>
<td>R_{13}</td>
<td>0.683221</td>
<td>0.585403</td>
<td>0.563175</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.536838</td>
<td>0.530932</td>
<td>0.530386</td>
<td>0.538</td>
</tr>
<tr>
<td>R_{14}</td>
<td>-0.385424</td>
<td>-0.399713</td>
<td>-0.402934</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.406565</td>
<td>-0.407499</td>
<td>-0.407576</td>
<td>-0.4079</td>
</tr>
<tr>
<td>R_{22}</td>
<td>1.11476</td>
<td>0.970999</td>
<td>0.943012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.901041</td>
<td>0.901403</td>
<td>0.901534</td>
<td>0.8996</td>
</tr>
<tr>
<td>R_{23}</td>
<td>0.104966</td>
<td>0.106276</td>
<td>0.106500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.106985</td>
<td>0.106838</td>
<td>0.106829</td>
<td>0.10677</td>
</tr>
<tr>
<td>R_{24}</td>
<td>0.624696</td>
<td>0.639928</td>
<td>0.642166</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.643589</td>
<td>0.644832</td>
<td>0.644934</td>
<td>0.6438</td>
</tr>
<tr>
<td>R_{33}</td>
<td>-0.28306</td>
<td>-0.121246</td>
<td>-0.119797</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.117575</td>
<td>-0.117581</td>
<td>-0.117582</td>
<td>-0.11786</td>
</tr>
<tr>
<td>R_{44}</td>
<td>0.116650</td>
<td>0.122996</td>
<td>0.124402</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.126617</td>
<td>0.126611</td>
<td>0.126609</td>
<td>0.12674</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>0.105057</td>
<td>0.104100</td>
<td>0.104194</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.104214</td>
<td>0.104202</td>
<td>0.104200</td>
<td>0.105</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>0.307664</td>
<td>0.273000</td>
<td>0.266281</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.253691</td>
<td>0.255573</td>
<td>0.255756</td>
<td>0.256</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>0.761272</td>
<td>0.796076</td>
<td>0.805559</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.810445</td>
<td>0.813485</td>
<td>0.813726</td>
<td>0.815</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>0.141349</td>
<td>0.118936</td>
<td>0.114662</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.108356</td>
<td>0.108404</td>
<td>0.108416</td>
<td>1.0828</td>
</tr>
</tbody>
</table>

\[ \alpha \quad 0.025594 \quad 0.002882 \quad 0.001030 \]
### Table XIX.E.

Singlet $L = 1$ results at $R = 2.25$

<table>
<thead>
<tr>
<th>matrix element</th>
<th>RN</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(-1)</td>
<td>0.466388</td>
<td>0.466079</td>
<td>0.466092</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1)</td>
<td>.465703</td>
<td>.466059</td>
<td>.466049</td>
<td>0.453</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(0)</td>
<td>-.418304</td>
<td>-.415824</td>
<td>-.415863</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.414633</td>
<td>-.415445</td>
<td>-.415518</td>
<td>-.4175</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>.320617</td>
<td>.306132</td>
<td>.304576</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.301213</td>
<td>.301432</td>
<td>.301468</td>
<td>.3105</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(0)</td>
<td>-.219806</td>
<td>-.251440</td>
<td>-.254331</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.238263</td>
<td>-.238403</td>
<td>-.238414</td>
<td>-.2410</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(+1)</td>
<td>.114630</td>
<td>.105963</td>
<td>.104155</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.101333</td>
<td>.101396</td>
<td>.101407</td>
<td>.10097</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(+1)</td>
<td>.182025</td>
<td>.193493</td>
<td>.195824</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.199681</td>
<td>.199389</td>
<td>.199363</td>
<td>.20162</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(-1)</td>
<td>-.094309</td>
<td>-.145067</td>
<td>-.160604</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-.204237</td>
<td>-.187319</td>
<td>-.185810</td>
<td>-.245</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>-.703210</td>
<td>-.691280</td>
<td>-.689205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-.686055</td>
<td>-.686266</td>
<td>-.686292</td>
<td>-.69787</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(+1)</td>
<td>.194153</td>
<td>.199319</td>
<td>.200526</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.202851</td>
<td>.202498</td>
<td>.202469</td>
<td>.20573</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(0)</td>
<td>-.147159</td>
<td>-.148141</td>
<td>-.148440</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.148620</td>
<td>-.148778</td>
<td>-.148784</td>
<td>-.1582</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-2)</td>
<td>.207165</td>
<td>.204872</td>
<td>.205290</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>.205013</td>
<td>.205187</td>
<td>.205194</td>
<td>.20</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>.334109</td>
<td>.317295</td>
<td>.314202</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.307926</td>
<td>.309044</td>
<td>.309143</td>
<td>.309</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-1)</td>
<td>.152653</td>
<td>.167030</td>
<td>.170544</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.174948</td>
<td>.175409</td>
<td>.175444</td>
<td>.176</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(+1)</td>
<td>.114556</td>
<td>.109871</td>
<td>.108880</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.107326</td>
<td>.107359</td>
<td>.107363</td>
<td>.10734</td>
</tr>
</tbody>
</table>

\[\alpha^a = 0.004317, \quad 0.000504, \quad 0.000183\]

\[\text{These values do not include } \alpha_{24}, \text{ for which } \alpha = 0.233017, 0.022294, \text{ and } 0.007854.\]
Table XIX.F.

Singlet L = 1 results at E = 4.00

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.143854</td>
<td>0.144136</td>
<td>0.144094</td>
<td>0.1414</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.144396</td>
<td>0.144104</td>
<td>0.144105</td>
<td>0.1414</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(0)</td>
<td>-0.226211</td>
<td>-0.223192</td>
<td>-0.222577</td>
<td>-0.22170</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.221409</td>
<td>-0.221603</td>
<td>-0.221621</td>
<td>-0.22170</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.142994</td>
<td>-0.149469</td>
<td>-0.149852</td>
<td>-0.149852</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.152773</td>
<td>-0.151005</td>
<td>-0.151012</td>
<td>-0.1507</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(-1)</td>
<td>-0.255716</td>
<td>-0.305710</td>
<td>-0.315885</td>
<td>-0.315885</td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.322710</td>
<td>-0.330688</td>
<td>-0.330743</td>
<td>-0.332</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(+1)</td>
<td>0.124892</td>
<td>0.125021</td>
<td>0.125049</td>
<td>0.125049</td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.125098</td>
<td>0.125092</td>
<td>0.125092</td>
<td>0.125092</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>-0.392803</td>
<td>-0.426643</td>
<td>-0.433528</td>
<td>-0.433528</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.445194</td>
<td>-0.444075</td>
<td>-0.445977</td>
<td>-0.445977</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>0.242200</td>
<td>0.268360</td>
<td>0.273706</td>
<td>0.273706</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.281595</td>
<td>0.281773</td>
<td>0.281746</td>
<td>0.2813</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>0.442740</td>
<td>0.442057</td>
<td>0.441836</td>
<td>0.441836</td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.441376</td>
<td>0.441446</td>
<td>0.444145</td>
<td>0.444145</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>-0.698771</td>
<td>-0.708533</td>
<td>-0.70932</td>
<td>-0.70932</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.713402</td>
<td>-0.711940</td>
<td>-0.711838</td>
<td>-0.711838</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(0)</td>
<td>0.549641</td>
<td>0.560781</td>
<td>0.563212</td>
<td>0.5643</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.566908</td>
<td>0.566964</td>
<td>0.566962</td>
<td>0.566962</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-2)</td>
<td>0.923455</td>
<td>0.924613</td>
<td>0.924366</td>
<td>0.924366</td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.926966</td>
<td>0.924443</td>
<td>0.924442</td>
<td>0.89</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.156056</td>
<td>0.153495</td>
<td>0.152884</td>
<td>0.152884</td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.152024</td>
<td>0.151975</td>
<td>0.151995</td>
<td>0.153</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-2)</td>
<td>0.187546</td>
<td>0.180434</td>
<td>0.225636</td>
<td>0.225636</td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.235584</td>
<td>0.234634</td>
<td>0.234649</td>
<td>0.234649</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(0)</td>
<td>0.505960</td>
<td>0.500378</td>
<td>0.499180</td>
<td>0.499180</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.497340</td>
<td>0.497319</td>
<td>0.497323</td>
<td>0.497323</td>
</tr>
<tr>
<td>$a$</td>
<td>0.005054</td>
<td>0.000523</td>
<td>0.000196</td>
<td>0.000196</td>
<td></td>
</tr>
</tbody>
</table>
Table XX.

Triplet $L = 1$, four channel results, calculated in the $1s$-$2s$-$2p$ approximation by integration scheme v. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BGG" column contains values from Reference 5.
Table XX.A.

Triplet L = 1 results at E = 0.81.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>RN</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁₁</td>
<td>(0)</td>
<td>0.411667</td>
<td>0.407857</td>
<td>0.407465</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.407630</td>
<td>0.407275</td>
<td>0.407248</td>
<td>0.4098</td>
</tr>
<tr>
<td>R₁₂</td>
<td>(0)</td>
<td>0.248548</td>
<td>0.217273</td>
<td>0.206927</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.182422</td>
<td>0.187254</td>
<td>0.187841</td>
<td>0.1860</td>
</tr>
<tr>
<td>R₁₃</td>
<td>(-1)</td>
<td>0.157099</td>
<td>0.622160</td>
<td>0.695401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.641116</td>
<td>0.768925</td>
<td>0.771059</td>
<td>0.699</td>
</tr>
<tr>
<td>R₁₄</td>
<td>(0)</td>
<td>0.294973</td>
<td>0.318264</td>
<td>0.329426</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.325375</td>
<td>0.339570</td>
<td>0.340706</td>
<td>0.3315</td>
</tr>
<tr>
<td>R₂₂</td>
<td>(0)</td>
<td>-1.15846</td>
<td>-1.588526</td>
<td>-1.478414</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.337908</td>
<td>-0.317850</td>
<td>-0.317554</td>
<td>-0.3167</td>
</tr>
<tr>
<td>R₂₃</td>
<td>(0)</td>
<td>-0.259663</td>
<td>-0.629204</td>
<td>-0.597214</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.518495</td>
<td>-0.527130</td>
<td>-0.527947</td>
<td>-0.5277</td>
</tr>
<tr>
<td>R₂₄</td>
<td>(+1)</td>
<td>-0.173059</td>
<td>-0.143637</td>
<td>-0.132793</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.115114</td>
<td>-0.112265</td>
<td>-0.112204</td>
<td>-0.11184</td>
</tr>
<tr>
<td>R₃₃</td>
<td>(0)</td>
<td>0.985434</td>
<td>0.760329</td>
<td>0.723011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.709383</td>
<td>0.680514</td>
<td>0.679590</td>
<td>0.6800</td>
</tr>
<tr>
<td>R₃₄</td>
<td>(+1)</td>
<td>-0.161431</td>
<td>-0.207998</td>
<td>-0.215331</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.224887</td>
<td>-0.223874</td>
<td>-0.223661</td>
<td>-0.22293</td>
</tr>
<tr>
<td>R₄₄</td>
<td>(+1)</td>
<td>-0.212479</td>
<td>-0.289033</td>
<td>-0.302030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.307890</td>
<td>-0.315748</td>
<td>-0.316172</td>
<td>-0.31550</td>
</tr>
<tr>
<td>Q₁₁</td>
<td>(+1)</td>
<td>0.172616</td>
<td>0.172618</td>
<td>0.172696</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.172680</td>
<td>0.172680</td>
<td>0.172679</td>
<td>0.17307</td>
</tr>
<tr>
<td>Q₁₂</td>
<td>(-1)</td>
<td>0.746152</td>
<td>0.709959</td>
<td>0.702212</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.641004</td>
<td>0.688450</td>
<td>0.692843</td>
<td>0.709</td>
</tr>
<tr>
<td>Q₁₃</td>
<td>(-1)</td>
<td>0.632746</td>
<td>0.664511</td>
<td>0.669608</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.629988</td>
<td>0.671408</td>
<td>0.675333</td>
<td>0.657</td>
</tr>
<tr>
<td>Q₂₂</td>
<td>(+1)</td>
<td>0.125894</td>
<td>0.306501</td>
<td>0.213204</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.130881</td>
<td>0.116643</td>
<td>0.116137</td>
<td>0.11596</td>
</tr>
<tr>
<td>α</td>
<td></td>
<td>0.289742</td>
<td>0.026339</td>
<td>0.009279</td>
<td></td>
</tr>
</tbody>
</table>
Table XX.B.

Triplet L = 1 results at E = 1.00

<table>
<thead>
<tr>
<th>matrix element</th>
<th>R_{N} \ 40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{11} (0)</td>
<td>0.583296</td>
<td>0.573793</td>
<td>0.573273</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.573266</td>
<td>0.573051</td>
<td>0.573009</td>
<td>0.5704</td>
</tr>
<tr>
<td>R_{12} (0)</td>
<td>-0.954322</td>
<td>-831196</td>
<td>-815691</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.786412</td>
<td>-0.792781</td>
<td>-0.793190</td>
<td>-0.7812</td>
</tr>
<tr>
<td>R_{13} (0)</td>
<td>-0.322825</td>
<td>-360184</td>
<td>-369138</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.378388</td>
<td>-0.382224</td>
<td>-0.382469</td>
<td>-0.3791</td>
</tr>
<tr>
<td>R_{14} (0)</td>
<td>-0.518199</td>
<td>-0.558019</td>
<td>-0.570036</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.583060</td>
<td>-0.588224</td>
<td>-0.588542</td>
<td>-0.5817</td>
</tr>
<tr>
<td>R_{22} (+1)</td>
<td>0.639849</td>
<td>0.532559</td>
<td>0.517260</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.495288</td>
<td>0.494324</td>
<td>0.494225</td>
<td>0.48984</td>
</tr>
<tr>
<td>R_{23} (+1)</td>
<td>0.174629</td>
<td>0.194550</td>
<td>0.198892</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.204633</td>
<td>0.204769</td>
<td>0.204744</td>
<td>0.20335</td>
</tr>
<tr>
<td>R_{24} (+1)</td>
<td>0.295830</td>
<td>0.304873</td>
<td>0.308731</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.314118</td>
<td>0.313868</td>
<td>0.313808</td>
<td>0.31094</td>
</tr>
<tr>
<td>R_{33} (0)</td>
<td>0.057337</td>
<td>0.251830</td>
<td>0.297166</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.364232</td>
<td>0.366213</td>
<td>0.366134</td>
<td>0.3618</td>
</tr>
<tr>
<td>R_{34} (0)</td>
<td>0.459391</td>
<td>0.731381</td>
<td>0.797709</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.902474</td>
<td>0.899835</td>
<td>0.899227</td>
<td>0.8896</td>
</tr>
<tr>
<td>R_{44} (+1)</td>
<td>0.160170</td>
<td>0.197676</td>
<td>0.207387</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.222139</td>
<td>0.222277</td>
<td>0.222244</td>
<td>0.22052</td>
</tr>
<tr>
<td>Q_{11} (+1)</td>
<td>0.136995</td>
<td>0.137122</td>
<td>0.137116</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.137090</td>
<td>0.137110</td>
<td>0.137110</td>
<td>0.13720</td>
</tr>
<tr>
<td>Q_{12} (-1)</td>
<td>0.120128</td>
<td>0.122363</td>
<td>0.122543</td>
<td>0.1219</td>
</tr>
<tr>
<td>(0)</td>
<td>0.721031</td>
<td>0.767240</td>
<td>0.777217</td>
<td></td>
</tr>
<tr>
<td>Q_{13} (+2)</td>
<td>0.230041</td>
<td>0.191428</td>
<td>0.183676</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.172449</td>
<td>0.172188</td>
<td>0.172182</td>
<td>1.7219</td>
</tr>
<tr>
<td>a</td>
<td>0.022562</td>
<td>0.002522</td>
<td>0.000931</td>
<td></td>
</tr>
</tbody>
</table>
Table XX.C.

Triplet $L = 1$ results at $E = 1.21$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_{40}$</th>
<th>$R_{120}$</th>
<th>$R_{200}$</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (0)</td>
<td>0.503707</td>
<td>0.501392</td>
<td>0.501466</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.501229</td>
<td>.501395</td>
<td>.501409</td>
<td>.5011</td>
</tr>
<tr>
<td>$R_{12}$ (0)</td>
<td>-.543028</td>
<td>-.501392</td>
<td>-.502583</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.490421</td>
<td>-.493701</td>
<td>-.493991</td>
<td>-.478</td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>-.218715</td>
<td>-.239750</td>
<td>-.244025</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.249006</td>
<td>-.250184</td>
<td>-.250275</td>
<td>-.2499</td>
</tr>
<tr>
<td>$R_{14}$ (0)</td>
<td>-.245452</td>
<td>-.271376</td>
<td>-.277503</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.284175</td>
<td>-.286108</td>
<td>-.286207</td>
<td>-.285</td>
</tr>
<tr>
<td>$R_{22}$ (+1)</td>
<td>.378948</td>
<td>3.503611</td>
<td>.349056</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.336276</td>
<td>3.503611</td>
<td>.336373</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (+1)</td>
<td>.106454</td>
<td>.122584</td>
<td>.125674</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.130346</td>
<td>.130227</td>
<td>.130216</td>
<td>.13002</td>
</tr>
<tr>
<td>$R_{24}$ (+1)</td>
<td>.115469</td>
<td>.128738</td>
<td>.131511</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.135249</td>
<td>.135560</td>
<td>.135584</td>
<td>.13529</td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>-.733497</td>
<td>-.640817</td>
<td>-.620268</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.587574</td>
<td>-.587624</td>
<td>-.587648</td>
<td>-.5887</td>
</tr>
<tr>
<td>$R_{34}$ (0)</td>
<td>.160576</td>
<td>.271567</td>
<td>.296832</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.339581</td>
<td>.337166</td>
<td>.336934</td>
<td>.3356</td>
</tr>
<tr>
<td>$R_{44}$ (0)</td>
<td>.706487</td>
<td>.870259</td>
<td>.867487</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.914747</td>
<td>.915301</td>
<td>.915348</td>
<td>.9143</td>
</tr>
<tr>
<td>$Q_{11}$ (+1)</td>
<td>.108624</td>
<td>.108568</td>
<td>.108568</td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.108577</td>
<td>.108568</td>
<td>.108569</td>
<td>.10862</td>
</tr>
<tr>
<td>$Q_{12}$ (0)</td>
<td>.106915</td>
<td>.102422</td>
<td>.101650</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.099116</td>
<td>.100167</td>
<td>.100267</td>
<td>.1000</td>
</tr>
<tr>
<td>$Q_{23}$ (-1)</td>
<td>.562839</td>
<td>.604954</td>
<td>.614878</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.622311</td>
<td>.627333</td>
<td>.627697</td>
<td>.629</td>
</tr>
<tr>
<td>$Q_{32}$ (+2)</td>
<td>.146916</td>
<td>.135158</td>
<td>.132607</td>
<td></td>
</tr>
<tr>
<td>(+2)</td>
<td>.128630</td>
<td>.128672</td>
<td>.128675</td>
<td>.12867</td>
</tr>
</tbody>
</table>

$\alpha$ .019316 .00145 .000524
Table XX.D.

Triplet \( L = 1 \) results at \( E = 1.44 \).

<table>
<thead>
<tr>
<th>matrix element</th>
<th>( R_N )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} )</td>
<td>(0)</td>
<td>0.464136</td>
<td>0.464000</td>
<td>0.464039</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.463964</td>
<td>0.463984</td>
<td>0.463995</td>
<td>0.4640</td>
</tr>
<tr>
<td>( R_{12} )</td>
<td>(0)</td>
<td>-3.5779</td>
<td>-3.58915</td>
<td>-3.55750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-3.49111</td>
<td>-3.50593</td>
<td>-3.50751</td>
<td>-3.508</td>
</tr>
<tr>
<td>( R_{13} )</td>
<td>(0)</td>
<td>-1.82834</td>
<td>-1.93718</td>
<td>-1.96107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-1.99300</td>
<td>-1.99764</td>
<td>-1.99792</td>
<td>-1.997</td>
</tr>
<tr>
<td>( R_{14} )</td>
<td>(0)</td>
<td>-1.64376</td>
<td>-1.79722</td>
<td>-1.83235</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-1.87423</td>
<td>-1.88262</td>
<td>-1.88332</td>
<td>-1.884</td>
</tr>
<tr>
<td>( R_{22} )</td>
<td>(+1)</td>
<td>0.282412</td>
<td>0.267080</td>
<td>0.263980</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.259092</td>
<td>0.259306</td>
<td>0.259336</td>
<td>0.25955</td>
</tr>
<tr>
<td>( R_{23} )</td>
<td>(+1)</td>
<td>0.090132</td>
<td>0.102817</td>
<td>0.105262</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.109080</td>
<td>0.108903</td>
<td>0.108885</td>
<td>0.10886</td>
</tr>
<tr>
<td>( R_{24} )</td>
<td>(0)</td>
<td>0.695921</td>
<td>0.778218</td>
<td>0.794842</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.818382</td>
<td>0.819822</td>
<td>0.819937</td>
<td>0.8208</td>
</tr>
<tr>
<td>( R_{33} )</td>
<td>(+1)</td>
<td>-1.37863</td>
<td>-1.3137</td>
<td>-1.29953</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-1.27690</td>
<td>-1.27734</td>
<td>-1.2793</td>
<td></td>
</tr>
<tr>
<td>( R_{34} )</td>
<td>(0)</td>
<td>0.201833</td>
<td>0.26997</td>
<td>0.285200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.312292</td>
<td>0.309610</td>
<td>0.309364</td>
<td>0.3090</td>
</tr>
<tr>
<td>( R_{44} )</td>
<td>(0)</td>
<td>0.581387</td>
<td>0.645604</td>
<td>0.660401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.684048</td>
<td>0.683960</td>
<td>0.683957</td>
<td>0.6843</td>
</tr>
<tr>
<td>( Q_{11} )</td>
<td>(0)</td>
<td>0.883871</td>
<td>0.884896</td>
<td>0.884937</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.884930</td>
<td>0.884896</td>
<td>0.884903</td>
<td>0.8853</td>
</tr>
<tr>
<td>( Q_{12} )</td>
<td>(-1)</td>
<td>0.762591</td>
<td>0.779550</td>
<td>0.727570</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.711400</td>
<td>0.16496</td>
<td>0.716968</td>
<td>0.716</td>
</tr>
<tr>
<td>( Q_{13} )</td>
<td>(-1)</td>
<td>0.370518</td>
<td>0.398867</td>
<td>0.406162</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.414245</td>
<td>0.416326</td>
<td>0.416455</td>
<td>0.416</td>
</tr>
<tr>
<td>( Q_{44} )</td>
<td>(+1)</td>
<td>0.997858</td>
<td>0.95733</td>
<td>0.934424</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.916581</td>
<td>0.916882</td>
<td>0.916923</td>
<td>0.91722</td>
</tr>
</tbody>
</table>

\( \alpha \)  
0.019925  
0.00350  
0.000854
Table XX.E.

Triplet $L = 1$ results at $E = 2.25$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>0</td>
<td>0.412242</td>
<td>0.411750</td>
<td>0.411810</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.411762</td>
<td>0.411789</td>
<td>0.411790</td>
<td>0.4118</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>0</td>
<td>-0.209635</td>
<td>-0.201804</td>
<td>-0.200682</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.198188</td>
<td>-0.198601</td>
<td>-0.198642</td>
<td>-0.1986</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>0</td>
<td>-0.146286</td>
<td>-0.155424</td>
<td>-0.155757</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.157260</td>
<td>-0.157300</td>
<td>-0.157317</td>
<td>-0.1577</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>+1</td>
<td>-0.800170</td>
<td>-0.836090</td>
<td>-0.850120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>-0.866959</td>
<td>-0.869364</td>
<td>-0.869570</td>
<td>-0.870</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>+1</td>
<td>0.169350</td>
<td>0.161791</td>
<td>0.160186</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.157637</td>
<td>0.157719</td>
<td>0.157732</td>
<td>0.15766</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>+1</td>
<td>0.123139</td>
<td>0.138038</td>
<td>0.14107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.145753</td>
<td>0.145400</td>
<td>0.145442</td>
<td>0.14653</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>0</td>
<td>0.193033</td>
<td>0.210730</td>
<td>0.214252</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.218280</td>
<td>0.219413</td>
<td>0.219583</td>
<td>0.2185</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>+1</td>
<td>-0.598304</td>
<td>-0.591165</td>
<td>-0.589789</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-0.587541</td>
<td>-0.587718</td>
<td>-0.587737</td>
<td>-0.59655</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>0</td>
<td>0.764461</td>
<td>0.613305</td>
<td>0.823559</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.844167</td>
<td>0.840018</td>
<td>0.839665</td>
<td>0.8500</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>0</td>
<td>0.438080</td>
<td>0.448081</td>
<td>0.450614</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.454917</td>
<td>0.454823</td>
<td>0.454823</td>
<td>0.4535</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>0</td>
<td>0.51488</td>
<td>0.514523</td>
<td>0.514575</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.514555</td>
<td>0.514562</td>
<td>0.514562</td>
<td>0.5148</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>-1</td>
<td>0.356921</td>
<td>0.342784</td>
<td>0.340237</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.334693</td>
<td>0.335888</td>
<td>0.335991</td>
<td>0.335</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>-1</td>
<td>0.112871</td>
<td>0.125626</td>
<td>0.128415</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.132125</td>
<td>0.132516</td>
<td>0.132543</td>
<td>0.133</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>+1</td>
<td>0.433406</td>
<td>0.424215</td>
<td>0.422204</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.418999</td>
<td>0.419049</td>
<td>0.419077</td>
<td>0.41917</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.011930</td>
<td>0.001383</td>
<td>0.000473</td>
<td></td>
</tr>
</tbody>
</table>
Table XX.F.

Triplet L = 1 results at E = 4.00.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.36321</td>
<td>0.363362</td>
<td>0.36337</td>
<td>0.3621</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.363494</td>
<td>0.363342</td>
<td>0.363343</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(0)</td>
<td>-1.149850</td>
<td>-1.148113</td>
<td>-1.147778</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-1.147070</td>
<td>-1.147228</td>
<td>-1.147239</td>
<td>-1.1469</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(-1)</td>
<td>-0.278996</td>
<td>-0.331332</td>
<td>-0.332153</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.357256</td>
<td>-0.340041</td>
<td>-0.340115</td>
<td>-0.344</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(-1)</td>
<td>-0.494872</td>
<td>-0.528064</td>
<td>-0.535059</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.35444</td>
<td>-0.544852</td>
<td>-0.544811</td>
<td>-0.546</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(+1)</td>
<td>0.133314</td>
<td>0.133607</td>
<td>0.133672</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.133781</td>
<td>0.133774</td>
<td>0.133774</td>
<td>0.13364</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>-0.365362</td>
<td>-0.406671</td>
<td>-0.414999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.428762</td>
<td>-0.427666</td>
<td>-0.427666</td>
<td>-0.4214</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>0.188393</td>
<td>0.213658</td>
<td>0.218803</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.226471</td>
<td>0.226593</td>
<td>0.226578</td>
<td>0.2262</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>0.475567</td>
<td>0.474864</td>
<td>0.474644</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.474259</td>
<td>0.474267</td>
<td>0.474265</td>
<td>0.47021</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>-0.540490</td>
<td>-0.550732</td>
<td>-0.552253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.555962</td>
<td>-0.554433</td>
<td>-0.554319</td>
<td>-0.5486</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(0)</td>
<td>0.567830</td>
<td>0.562931</td>
<td>0.578221</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.581091</td>
<td>0.581216</td>
<td>0.581215</td>
<td>0.5790</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(0)</td>
<td>0.242652</td>
<td>0.242748</td>
<td>0.242730</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.242922</td>
<td>0.242735</td>
<td>0.242735</td>
<td>0.2412</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.159787</td>
<td>0.156240</td>
<td>0.155412</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.154308</td>
<td>0.154190</td>
<td>0.154212</td>
<td>0.154</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-2)</td>
<td>0.315056</td>
<td>0.361038</td>
<td>0.368395</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.372619</td>
<td>0.380417</td>
<td>0.380457</td>
<td>0.38</td>
</tr>
<tr>
<td>$Q_{25}$</td>
<td>(+1)</td>
<td>0.167576</td>
<td>0.166279</td>
<td>0.165972</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.165530</td>
<td>0.165524</td>
<td>0.165525</td>
<td>0.16547</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.002333</td>
<td>0.000610</td>
<td>0.000220</td>
<td></td>
</tr>
</tbody>
</table>
Table XXI.

Results of calculations on the singlet \( L = 2 \) state at \( E = 0.81 \) in
the 1s-2s-2p exchange approximation with step sizes \( \Delta_B = 0.025 \) and
\( \Delta_Y = 0.0125 \). Range of integration is 40. Assuming the Quadratic
Rule to hold, extrapolation to zero step size is included and the
fractional error due to finite step size \( \Delta_B \) estimated. The numbers
in parentheses give the power of ten by which the matrix elements
should be multiplied.

<table>
<thead>
<tr>
<th>Matrix Element M</th>
<th>( M(\Delta_B) )</th>
<th>( M(\Delta_Y) )</th>
<th>( M(0)^a )</th>
<th>( q^b )</th>
<th>( r^b \Delta_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} ) (-)</td>
<td>-0.131666</td>
<td>-0.131743</td>
<td>-0.131769</td>
<td>0.164 (+1)</td>
<td>0.000782</td>
</tr>
<tr>
<td>( R_{12} ) (0)</td>
<td>-0.681671</td>
<td>-0.682083</td>
<td>-0.682220</td>
<td>0.879 (0)</td>
<td>0.000805</td>
</tr>
<tr>
<td>( R_{13} ) (-2)</td>
<td>0.110993</td>
<td>0.111056</td>
<td>0.111077</td>
<td>-1.34 (+2)</td>
<td>-0.000756</td>
</tr>
<tr>
<td>( R_{14} ) (+1)</td>
<td>-0.338505</td>
<td>-0.338696</td>
<td>-0.338760</td>
<td>0.405 (1)</td>
<td>-0.000752</td>
</tr>
<tr>
<td>( R_{22} ) (0)</td>
<td>-0.161462</td>
<td>-0.161685</td>
<td>-0.161759</td>
<td>0.476 (0)</td>
<td>-0.001838</td>
</tr>
<tr>
<td>( R_{23} ) (-1)</td>
<td>0.635415</td>
<td>0.635749</td>
<td>0.635860</td>
<td>-0.710 (+1)</td>
<td>-0.000698</td>
</tr>
<tr>
<td>( R_{24} ) (+1)</td>
<td>-0.258633</td>
<td>-0.258736</td>
<td>-0.258770</td>
<td>0.220 (+1)</td>
<td>-0.000531</td>
</tr>
<tr>
<td>( R_{33} ) (+2)</td>
<td>-0.876928</td>
<td>-0.877436</td>
<td>-0.877605</td>
<td>0.108 (+3)</td>
<td>-0.000772</td>
</tr>
<tr>
<td>( R_{34} ) (+2)</td>
<td>0.269860</td>
<td>0.270116</td>
<td>0.270068</td>
<td>-0.333 (+2)</td>
<td>-0.000770</td>
</tr>
<tr>
<td>( R_{44} ) (1)</td>
<td>-0.904464</td>
<td>-0.904948</td>
<td>-0.905108</td>
<td>102 (+2)</td>
<td>0.000706</td>
</tr>
<tr>
<td>( Q_{11} ) (-1)</td>
<td>0.429522</td>
<td>0.459479</td>
<td>0.459465</td>
<td>0.917 (-2)</td>
<td>0.000125</td>
</tr>
<tr>
<td>( Q_{12} ) (-1)</td>
<td>0.547460</td>
<td>0.547438</td>
<td>0.547431</td>
<td>0.469 (-2)</td>
<td>0.000054</td>
</tr>
<tr>
<td>( Q_{13} ) (0)</td>
<td>0.113600</td>
<td>0.113596</td>
<td>0.113595</td>
<td>0.853 (-2)</td>
<td>0.000047</td>
</tr>
<tr>
<td>( Q_{22} ) (+2)</td>
<td>0.139245</td>
<td>0.139243</td>
<td>0.139242</td>
<td>427 (0)</td>
<td>0.000019</td>
</tr>
</tbody>
</table>

\(^a\) Extrapolated to zero step size by Quadratic Rule in the form
\( M(0) = M(\Delta_B) - 4 \frac{2}{\Delta_B} [M(\Delta_B/2) - M(\Delta_Y)] \)

\(^b\) Numbers in parentheses give the power of ten by which the preceding
number should be multiplied.
Table XXII.

Singlet $L = 2$, four channel results, calculated in the $1s-2s-2p$ approximation by integration scheme v.

For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BSS" column contains values from Reference 5.
Table XXII.A.

Singlet $L = 2$ results at $E = 0.81$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(+1)</td>
<td>-0.131666</td>
<td>-0.136330</td>
<td>-0.141036</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.138995</td>
<td>-0.144824</td>
<td>-0.144566</td>
<td>-0.12834</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(+1)</td>
<td>-0.068167</td>
<td>-0.153476</td>
<td>-0.176074</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.189219</td>
<td>-0.205896</td>
<td>-0.206199</td>
<td>-0.18061</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(+2)</td>
<td>0.110993</td>
<td>0.115284</td>
<td>0.118859</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.116022</td>
<td>0.121159</td>
<td>0.121042</td>
<td>0.10695</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(+1)</td>
<td>-0.338505</td>
<td>-0.387597</td>
<td>-0.407205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.429828</td>
<td>-0.429892</td>
<td>-0.427983</td>
<td>-0.37558</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(+1)</td>
<td>-0.016146</td>
<td>-0.139155</td>
<td>-0.183448</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.236666</td>
<td>-0.255242</td>
<td>-0.254855</td>
<td>-0.21310</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(+2)</td>
<td>0.063541</td>
<td>0.131822</td>
<td>0.149509</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.169477</td>
<td>0.173659</td>
<td>0.173011</td>
<td>0.15004</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(+1)</td>
<td>-0.258633</td>
<td>-0.493489</td>
<td>-0.558677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.669126</td>
<td>-0.656474</td>
<td>-0.651994</td>
<td>-0.56676</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+2)</td>
<td>-0.876928</td>
<td>-0.913459</td>
<td>-0.940073</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>-0.920213</td>
<td>-0.953986</td>
<td>-0.952521</td>
<td>-0.82956</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(+2)</td>
<td>0.269860</td>
<td>0.310968</td>
<td>0.326231</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.345178</td>
<td>0.343093</td>
<td>0.341420</td>
<td>0.29565</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(+2)</td>
<td>-0.090447</td>
<td>-0.115714</td>
<td>-0.123423</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>-0.125440</td>
<td>-0.132640</td>
<td>-0.132562</td>
<td>-0.11605</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.459522</td>
<td>0.453769</td>
<td>0.453639</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.453569</td>
<td>0.453944</td>
<td>0.453920</td>
<td>0.470</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.547460</td>
<td>0.581547</td>
<td>0.586498</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.542195</td>
<td>0.591059</td>
<td>0.594970</td>
<td>0.581</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>0.113600</td>
<td>0.110788</td>
<td>0.110008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.103433</td>
<td>0.108232</td>
<td>0.108639</td>
<td>0.1095</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(+2)</td>
<td>0.139245</td>
<td>0.203189</td>
<td>0.212488</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.220065</td>
<td>0.222831</td>
<td>0.222941</td>
<td>0.22204</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.186911</td>
<td>0.018642</td>
<td>0.006566</td>
<td></td>
</tr>
</tbody>
</table>
Table XXII.B.

Singlet $L = 2$ results at $E = 1.00$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.143937</td>
<td>0.144300</td>
<td>0.144308</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td></td>
<td></td>
<td>0.1447</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>0.612780</td>
<td>0.648572</td>
<td>0.657612</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td>0.671</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.363898</td>
<td>-0.363221</td>
<td>-0.362483</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.361114</td>
<td>-0.361324</td>
<td>-0.361355</td>
<td>-0.3623</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(0)</td>
<td>0.219344</td>
<td>0.227021</td>
<td>0.228234</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td></td>
<td></td>
<td>0.2294</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>0.516284</td>
<td>0.540940</td>
<td>0.542366</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td></td>
<td></td>
<td>0.5420</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>0.461696</td>
<td>0.465467</td>
<td>0.464388</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td></td>
<td></td>
<td>0.4618</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>-0.566813</td>
<td>-0.423835</td>
<td>-0.391314</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.347663</td>
<td>-0.342890</td>
<td>-0.342653</td>
<td>-0.3424</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>0.126239</td>
<td>0.133256</td>
<td>0.134495</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td></td>
<td></td>
<td></td>
<td>0.13545</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>-0.519226</td>
<td>-0.522295</td>
<td>-0.520166</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.528307</td>
<td>-0.517745</td>
<td>-0.516854</td>
<td>-0.5159</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(+1)</td>
<td>-0.103577</td>
<td>-0.112245</td>
<td>-0.113645</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-0.115310</td>
<td>-0.115445</td>
<td>-0.115439</td>
<td>-0.11545</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.651970</td>
<td>0.652702</td>
<td>0.653054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.652562</td>
<td>0.653103</td>
<td>0.653039</td>
<td>0.654</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.789022</td>
<td>0.811040</td>
<td>0.814951</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.803999</td>
<td>0.819484</td>
<td>0.820751</td>
<td>0.823</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>0.254885</td>
<td>0.253814</td>
<td>0.253456</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.250842</td>
<td>0.252571</td>
<td>0.252725</td>
<td>0.2532</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(+1)</td>
<td>0.335405</td>
<td>0.323606</td>
<td>0.320422</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.315114</td>
<td>0.315178</td>
<td>0.315212</td>
<td>0.31518</td>
</tr>
</tbody>
</table>

| $\alpha$      | .050527| .005527| .001981|       |
Table XXII.C.

Singlet $L = 2$ results at $E = 1.44$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.112055</td>
<td>0.112557</td>
<td>0.112625</td>
<td>0.1125</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.112648</td>
<td>0.112622</td>
<td>0.112624</td>
<td>0.1125</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>0.055183</td>
<td>0.140435</td>
<td>0.159104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.187548</td>
<td>0.188690</td>
<td>0.188739</td>
<td>0.189</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.470916</td>
<td>-0.471287</td>
<td>-0.471416</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.470918</td>
<td>-0.471200</td>
<td>-0.471232</td>
<td>-0.4712</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(0)</td>
<td>0.169223</td>
<td>0.170407</td>
<td>0.170480</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.171240</td>
<td>0.170745</td>
<td>0.170705</td>
<td>0.1707</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>0.754087</td>
<td>0.727641</td>
<td>0.721362</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.711500</td>
<td>0.711318</td>
<td>0.711314</td>
<td>0.7111</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>0.344258</td>
<td>0.352647</td>
<td>0.353470</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.354254</td>
<td>0.354123</td>
<td>0.354086</td>
<td>0.3541</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(-1)</td>
<td>-0.170090</td>
<td>0.478278</td>
<td>0.610040</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.798842</td>
<td>0.807754</td>
<td>0.808319</td>
<td>0.809</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>0.109989</td>
<td>0.112868</td>
<td>0.113436</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.114260</td>
<td>0.114265</td>
<td>0.114262</td>
<td>0.11423</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(0)</td>
<td>-0.392730</td>
<td>-0.378332</td>
<td>-0.374817</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.371742</td>
<td>-0.369411</td>
<td>-0.369219</td>
<td>-0.3691</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.350594</td>
<td>0.350812</td>
<td>0.351041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.351130</td>
<td>0.350965</td>
<td>0.350982</td>
<td>0.351</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.220157</td>
<td>0.236836</td>
<td>0.240199</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.243200</td>
<td>0.244973</td>
<td>0.245115</td>
<td>0.245</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>0.291760</td>
<td>0.290195</td>
<td>0.289949</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.289184</td>
<td>0.289383</td>
<td>0.289412</td>
<td>0.2895</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(+1)</td>
<td>0.227691</td>
<td>0.216906</td>
<td>0.214413</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.210581</td>
<td>0.210469</td>
<td>0.210466</td>
<td>0.21036</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.016375</td>
<td>0.001674</td>
<td>0.000599</td>
<td></td>
</tr>
</tbody>
</table>
Table XXII.D.

Singlet L = 2 results at E = 2.25.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>( R_N )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{11}</td>
<td>(-1)</td>
<td>0.479871</td>
<td>0.476654</td>
<td>0.477296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.47955</td>
<td>0.477207</td>
<td>0.477188</td>
<td>0.474</td>
</tr>
<tr>
<td>R_{12}</td>
<td>(-1)</td>
<td>-0.578956</td>
<td>-0.515485</td>
<td>-0.502704</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.481831</td>
<td>-0.482589</td>
<td>-0.482636</td>
<td>-0.482</td>
</tr>
<tr>
<td>R_{13}</td>
<td>(0)</td>
<td>-0.344337</td>
<td>-0.345330</td>
<td>-0.345711</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.345845</td>
<td>-0.346073</td>
<td>-0.346078</td>
<td>-0.3461</td>
</tr>
<tr>
<td>R_{14}</td>
<td>(-1)</td>
<td>0.734183</td>
<td>0.717629</td>
<td>0.714660</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.712506</td>
<td>0.710129</td>
<td>0.710016</td>
<td>0.710</td>
</tr>
<tr>
<td>R_{22}</td>
<td>(0)</td>
<td>0.783834</td>
<td>0.773151</td>
<td>0.770766</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.767100</td>
<td>0.767030</td>
<td>0.767027</td>
<td>0.7669</td>
</tr>
<tr>
<td>R_{23}</td>
<td>(0)</td>
<td>0.129479</td>
<td>0.129925</td>
<td>0.129674</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.128930</td>
<td>0.129067</td>
<td>0.129066</td>
<td>0.1290</td>
</tr>
<tr>
<td>R_{24}</td>
<td>(-1)</td>
<td>0.518284</td>
<td>0.805988</td>
<td>0.864879</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.951506</td>
<td>0.953746</td>
<td>0.953810</td>
<td>0.955</td>
</tr>
<tr>
<td>R_{33}</td>
<td>(+1)</td>
<td>0.120328</td>
<td>0.121150</td>
<td>0.121282</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.121487</td>
<td>0.121490</td>
<td>0.121489</td>
<td>0.12149</td>
</tr>
<tr>
<td>R_{34}</td>
<td>(0)</td>
<td>-0.296474</td>
<td>-0.292685</td>
<td>-0.291647</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.290701</td>
<td>-0.289900</td>
<td>-0.289838</td>
<td>-0.2899</td>
</tr>
<tr>
<td>R_{44}</td>
<td>(-1)</td>
<td>0.593723</td>
<td>0.623919</td>
<td>0.633896</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.651087</td>
<td>0.650650</td>
<td>0.650615</td>
<td>0.648</td>
</tr>
<tr>
<td>Q_{11}</td>
<td>(-2)</td>
<td>0.492356</td>
<td>0.489097</td>
<td>0.489486</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.489210</td>
<td>0.489425</td>
<td>0.489389</td>
<td>0.49</td>
</tr>
<tr>
<td>Q_{12}</td>
<td>(-2)</td>
<td>0.216481</td>
<td>0.167559</td>
<td>0.158747</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.145031</td>
<td>0.145496</td>
<td>0.145525</td>
<td>0.15</td>
</tr>
<tr>
<td>Q_{13}</td>
<td>(-1)</td>
<td>0.938750</td>
<td>0.939452</td>
<td>0.940855</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.941113</td>
<td>0.941988</td>
<td>0.942011</td>
<td>0.942</td>
</tr>
<tr>
<td>Q_{22}</td>
<td>(+1)</td>
<td>0.123455</td>
<td>0.120844</td>
<td>0.120249</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.119336</td>
<td>0.119314</td>
<td>0.119314</td>
<td>0.11929</td>
</tr>
</tbody>
</table>

\( a \) | 0.006521 | 0.000747 | 0.000268 |
Table XXIII.

Triplet L = 2, four channel results, calculated in the 1s-2s-2p approximation by integration scheme v. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated R_N. The second row entries give the results from the projection procedure applied at that R_N. At the bottom of each column are the values of the asymmetry parameter for that projected R matrix. The "BSS" column contains values from Reference 5.
Table XXIII.A.

Triplet $L = 2$ results at $E = 0.81$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_n$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(-1)</td>
<td>0.685017</td>
<td>0.684874</td>
<td>0.684888</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.684793</td>
<td>.684860</td>
<td>.684848</td>
<td>0.686</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>-.439492</td>
<td>-.420448</td>
<td>-.413120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-.379091</td>
<td>-.397666</td>
<td>-.398997</td>
<td>-.415</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(-2)</td>
<td>-.306851</td>
<td>-.700776</td>
<td>-.794502</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>-.875463</td>
<td>-.938849</td>
<td>-.943586</td>
<td>-.98</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(-1)</td>
<td>-.118518</td>
<td>-.197510</td>
<td>-.210476</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-.221179</td>
<td>-.229745</td>
<td>-.230648</td>
<td>-.243</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>.778161</td>
<td>.742107</td>
<td>.716130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.667041</td>
<td>.668244</td>
<td>.668512</td>
<td>.6684</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(+1)</td>
<td>.115518</td>
<td>.124846</td>
<td>.125402</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.129590</td>
<td>.125991</td>
<td>.125674</td>
<td>.12533</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>-.747541</td>
<td>-.561306</td>
<td>-.519386</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.502183</td>
<td>-.459414</td>
<td>-.456497</td>
<td>-.4545</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(0)</td>
<td>-.261945</td>
<td>-.009497</td>
<td>.050040</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.133895</td>
<td>.146216</td>
<td>.146420</td>
<td>.1447</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>.339226</td>
<td>.475089</td>
<td>.503084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.511839</td>
<td>.542727</td>
<td>.544725</td>
<td>.5451</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(+1)</td>
<td>-.081472</td>
<td>-.105557</td>
<td>-.109189</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>-.113002</td>
<td>-.113984</td>
<td>-.114020</td>
<td>-.11398</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>.857250</td>
<td>.857864</td>
<td>.857927</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.857692</td>
<td>.857915</td>
<td>.857906</td>
<td>.861</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-2)</td>
<td>.388188</td>
<td>.318879</td>
<td>.307309</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>.262625</td>
<td>.284084</td>
<td>.285556</td>
<td>.31</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-2)</td>
<td>.669213</td>
<td>.731229</td>
<td>.741058</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>.750436</td>
<td>.760099</td>
<td>.761367</td>
<td>.83</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(+2)</td>
<td>1.30974</td>
<td>1.08525</td>
<td>1.01636</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>.909187</td>
<td>.903163</td>
<td>.903194</td>
<td>.90320</td>
</tr>
<tr>
<td>$a$</td>
<td></td>
<td>.204822</td>
<td>.019712</td>
<td>.006879</td>
<td></td>
</tr>
</tbody>
</table>
Table XXIII.B.

Triplet L = 2 results at E = 1.00.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>-1</td>
<td>0.699692</td>
<td>0.693524</td>
<td>0.693453</td>
<td>0.695</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.693728</td>
<td>0.693379</td>
<td>0.693383</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>0</td>
<td>-0.090088</td>
<td>-0.099358</td>
<td>-1.01293</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-1.102917</td>
<td>-1.104028</td>
<td>-1.04118</td>
<td>-1.040</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>0</td>
<td>0.273660</td>
<td>0.277048</td>
<td>0.276005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.273005</td>
<td>0.274006</td>
<td>0.274062</td>
<td>0.2716</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>-1</td>
<td>-0.856347</td>
<td>-0.944994</td>
<td>-0.958483</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>-0.989621</td>
<td>-0.983657</td>
<td>-0.983124</td>
<td>-0.977</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>0</td>
<td>1.06329</td>
<td>0.966216</td>
<td>0.937946</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.891601</td>
<td>0.892226</td>
<td>0.892282</td>
<td>0.8925</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>+1</td>
<td>0.070048</td>
<td>0.105862</td>
<td>0.113774</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.126795</td>
<td>0.125513</td>
<td>0.125442</td>
<td>0.12522</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>-1</td>
<td>-0.340068</td>
<td>0.530939</td>
<td>0.114644</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.107859</td>
<td>0.193733</td>
<td>0.198238</td>
<td>0.208</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>+1</td>
<td>-0.705410</td>
<td>-0.698139</td>
<td>-0.695563</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>-0.691878</td>
<td>-0.691094</td>
<td>-0.691125</td>
<td>-0.68871</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>+1</td>
<td>0.125015</td>
<td>0.131110</td>
<td>0.132682</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.138746</td>
<td>0.135804</td>
<td>0.135573</td>
<td>0.13483</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>0</td>
<td>-0.533810</td>
<td>-0.537412</td>
<td>-0.537014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.535221</td>
<td>-0.536137</td>
<td>-0.536159</td>
<td>-0.5346</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>-1</td>
<td>0.930458</td>
<td>0.932580</td>
<td>0.932811</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.932627</td>
<td>0.932753</td>
<td>0.932740</td>
<td>0.934</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>-1</td>
<td>0.264391</td>
<td>0.228217</td>
<td>0.220349</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.204996</td>
<td>0.208633</td>
<td>0.208994</td>
<td>0.211</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>-1</td>
<td>0.392334</td>
<td>0.443200</td>
<td>0.449169</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.455688</td>
<td>0.460136</td>
<td>0.460496</td>
<td>0.458</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>+2</td>
<td>0.330547</td>
<td>0.317189</td>
<td>0.313065</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+2</td>
<td>0.306298</td>
<td>0.306226</td>
<td>0.306246</td>
<td>0.30629</td>
</tr>
</tbody>
</table>

$\alpha^a \quad 0.49794 \quad 0.005352 \quad 0.001914$

$^a$ These values do not include $R_{34}$, for which $\alpha = 1.46251$, 0.082521, and 0.028425.
Table XXIII.C.

Triplet L = 2 results at E = 1.44.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(0)</td>
<td>0.111444</td>
<td>0.111668</td>
<td>0.111706</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.111725</td>
<td>0.111693</td>
<td>0.111693</td>
<td>0.1117</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>-.979476</td>
<td>-.901547</td>
<td>-.884887</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-.855836</td>
<td>-.858418</td>
<td>-.858652</td>
<td>-.859</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-.202071</td>
<td>-.206754</td>
<td>-.207775</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.208504</td>
<td>-.208670</td>
<td>-.208699</td>
<td>-.2087</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(-1)</td>
<td>-.114954</td>
<td>-.151324</td>
<td>-.160530</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-.168510</td>
<td>-.172317</td>
<td>-.172649</td>
<td>-.175</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>.883020</td>
<td>.866560</td>
<td>.863110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.858084</td>
<td>.857862</td>
<td>.857854</td>
<td>.8577</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>.221843</td>
<td>.167331</td>
<td>.155107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>.135216</td>
<td>.135772</td>
<td>.135777</td>
<td>.1362</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(-1)</td>
<td>.012801</td>
<td>.509556</td>
<td>.612714</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.763632</td>
<td>.769137</td>
<td>.769378</td>
<td>.769</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(+1)</td>
<td>.300866</td>
<td>.302723</td>
<td>.303009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.303326</td>
<td>.303360</td>
<td>.303359</td>
<td>.30325</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>-.377119</td>
<td>-.371272</td>
<td>-.369607</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-.372454</td>
<td>-.367531</td>
<td>-.367134</td>
<td>-.3669</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(-1)</td>
<td>.313311</td>
<td>.322854</td>
<td>.332075</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.352021</td>
<td>.350789</td>
<td>.350730</td>
<td>.351</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>.936798</td>
<td>.938751</td>
<td>.938734</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.938743</td>
<td>.938649</td>
<td>.938654</td>
<td>.938</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>.416848</td>
<td>.378145</td>
<td>.370312</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.355756</td>
<td>.358123</td>
<td>.358325</td>
<td>.358</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(-1)</td>
<td>.477682</td>
<td>.515847</td>
<td>.525737</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>.536062</td>
<td>.536979</td>
<td>.537168</td>
<td>.539</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(+1)</td>
<td>.920018</td>
<td>.906961</td>
<td>.903435</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>.897902</td>
<td>.897549</td>
<td>.897538</td>
<td>.89735</td>
</tr>
</tbody>
</table>

| $\alpha$      | .053124  | .005890  | .002114 |         |
Table XXIII.D.

Triplet L = 2 results at E = 2.25.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>R_N</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{11} (0)</td>
<td></td>
<td>.126829</td>
<td>.126599</td>
<td>.126632</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>.126604</td>
<td>.126625</td>
<td>.126624</td>
</tr>
<tr>
<td>R_{12} (-1)</td>
<td></td>
<td>-.960753</td>
<td>-.969634</td>
<td>-.962046</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>-.948377</td>
<td>-.949891</td>
<td>-.950005</td>
</tr>
<tr>
<td>R_{13} (0)</td>
<td></td>
<td>-.1364839</td>
<td>-.136443</td>
<td>-.137083</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>-.137616</td>
<td>-.137794</td>
<td>-.137790</td>
</tr>
<tr>
<td>R_{14} (-1)</td>
<td></td>
<td>-.138026</td>
<td>-.139625</td>
<td>-.139650</td>
<td>-.140</td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>-.138026</td>
<td>-.139625</td>
<td>-.139650</td>
</tr>
<tr>
<td>R_{22} (0)</td>
<td></td>
<td>.825902</td>
<td>.818188</td>
<td>.816492</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>.813932</td>
<td>.813854</td>
<td>.813852</td>
</tr>
<tr>
<td>R_{23} (0)</td>
<td></td>
<td>.134770</td>
<td>.124777</td>
<td>.122366</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>.118347</td>
<td>.118491</td>
<td>.118484</td>
</tr>
<tr>
<td>R_{24} (-1)</td>
<td></td>
<td>.319750</td>
<td>.319750</td>
<td>.319750</td>
<td>.319750</td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>.441965</td>
<td>.444526</td>
<td>.444602</td>
</tr>
<tr>
<td>R_{33} (+1)</td>
<td></td>
<td>.159038</td>
<td>.159038</td>
<td>.159038</td>
<td>.159038</td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td></td>
<td>.160024</td>
<td>.160024</td>
<td>.160024</td>
</tr>
<tr>
<td>R_{34} (0)</td>
<td></td>
<td>-.223112</td>
<td>-.223109</td>
<td>-.222381</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>-.222203</td>
<td>-.221164</td>
<td>-.221082</td>
</tr>
<tr>
<td>R_{44} (0)</td>
<td></td>
<td>.197303</td>
<td>.197303</td>
<td>.197303</td>
<td>.197303</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>.197359</td>
<td>.197733</td>
<td>.197731</td>
</tr>
<tr>
<td>Q_{11} (-1)</td>
<td></td>
<td>.846924</td>
<td>.845376</td>
<td>.845592</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>.845400</td>
<td>.845524</td>
<td>.845527</td>
</tr>
<tr>
<td>Q_{12} (-1)</td>
<td></td>
<td>.332176</td>
<td>.311813</td>
<td>.307824</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>.300605</td>
<td>.301556</td>
<td>.301636</td>
</tr>
<tr>
<td>Q_{13} (-1)</td>
<td></td>
<td>.332065</td>
<td>.346557</td>
<td>.351259</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td></td>
<td>.356109</td>
<td>.357206</td>
<td>.357180</td>
</tr>
<tr>
<td>Q_{14} (+1)</td>
<td></td>
<td>.393212</td>
<td>.389371</td>
<td>.388460</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td></td>
<td>.387069</td>
<td>.387003</td>
<td>.387002</td>
</tr>
<tr>
<td>a</td>
<td>0.020112</td>
<td>.002263</td>
<td>.000816</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Singlet $L = 3$, four channel results, calculated in the $1s$-$2s$-$2p$ approximation by integration scheme $v$. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $R$ matrix. The "BSS" column contains values from Reference 5.
Table XXIV.A.
Singlet L = 3 results at E = 1.00.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{11}$</td>
<td>-1</td>
<td>0.359346</td>
<td>0.360620</td>
<td>0.360568</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.360257</td>
<td>0.360547</td>
<td>0.360528</td>
<td>0.3600</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>-2</td>
<td>-0.850202</td>
<td>-0.375243</td>
<td>-0.273670</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>-0.116618</td>
<td>-0.121497</td>
<td>-0.116891</td>
<td>-0.12</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>0</td>
<td>-0.101641</td>
<td>-0.103093</td>
<td>-0.103057</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.102578</td>
<td>-0.103054</td>
<td>-0.103103</td>
<td>-0.1031</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>-1</td>
<td>0.193796</td>
<td>0.186473</td>
<td>0.187388</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.188208</td>
<td>0.186309</td>
<td>0.186456</td>
<td>0.186</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>-1</td>
<td>-0.108210</td>
<td>0.104554</td>
<td>0.137847</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.403022</td>
<td>0.223127</td>
<td>0.199525</td>
<td>0.185</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>0</td>
<td>0.715033</td>
<td>0.697692</td>
<td>0.691387</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.673750</td>
<td>0.679102</td>
<td>0.679784</td>
<td>0.6801</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>0</td>
<td>-0.741246</td>
<td>-0.710322</td>
<td>-0.701672</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.626888</td>
<td>-0.679493</td>
<td>-0.683762</td>
<td>-0.6861</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>0</td>
<td>0.296617</td>
<td>0.385577</td>
<td>0.404147</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.435044</td>
<td>0.431695</td>
<td>0.431252</td>
<td>0.4310</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>0</td>
<td>0.162455</td>
<td>0.170516</td>
<td>0.171887</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.163219</td>
<td>0.172697</td>
<td>0.173485</td>
<td>0.1738</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>-2</td>
<td>0.810856</td>
<td>0.815513</td>
<td>0.815253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>0.814917</td>
<td>0.815040</td>
<td>0.815000</td>
<td>0.31</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>-1</td>
<td>0.109732</td>
<td>0.105452</td>
<td>0.104530</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.102351</td>
<td>0.102697</td>
<td>0.102813</td>
<td>103</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>-1</td>
<td>0.341074</td>
<td>0.350426</td>
<td>0.350164</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0.346222</td>
<td>0.351328</td>
<td>0.351686</td>
<td>352</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>+1</td>
<td>0.575378</td>
<td>0.488018</td>
<td>0.466980</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.377687</td>
<td>0.427150</td>
<td>0.431271</td>
<td>0.43353</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>0.115330</td>
<td>0.010683</td>
<td>0.003683</td>
<td></td>
</tr>
</tbody>
</table>
Table XXIV.B.

Singlet $L = 3$ results at $E = 1.44$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(-1)</td>
<td>0.401331</td>
<td>0.403241</td>
<td>0.403423</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.403587</td>
<td>0.403339</td>
<td>0.40351</td>
<td>0.403312</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>0.105321</td>
<td>0.15237</td>
<td>0.163026</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.171612</td>
<td>0.177227</td>
<td>0.177591</td>
<td>0.178</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.204567</td>
<td>-0.203839</td>
<td>-0.203895</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.203267</td>
<td>-0.203642</td>
<td>-0.203675</td>
<td>-0.2037</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(0)</td>
<td>0.644351</td>
<td>0.662915</td>
<td>0.663912</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.667426</td>
<td>0.665732</td>
<td>0.665861</td>
<td>0.666</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>0.277692</td>
<td>0.286585</td>
<td>0.287722</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.292762</td>
<td>0.289609</td>
<td>0.289237</td>
<td>0.2889</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>0.434450</td>
<td>0.43049</td>
<td>0.429024</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.426794</td>
<td>0.426573</td>
<td>0.426568</td>
<td>0.4265</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(0)</td>
<td>-0.465527</td>
<td>-0.428651</td>
<td>-0.420476</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.388792</td>
<td>-0.405737</td>
<td>-0.407119</td>
<td>-0.4079</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(0)</td>
<td>0.413420</td>
<td>0.445998</td>
<td>0.452671</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.462966</td>
<td>0.462829</td>
<td>0.462802</td>
<td>0.4626</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>0.420680</td>
<td>0.423008</td>
<td>0.427156</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.423495</td>
<td>0.434522</td>
<td>0.435355</td>
<td>0.436</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(0)</td>
<td>-0.629830</td>
<td>-0.673176</td>
<td>-0.681120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.693413</td>
<td>-0.692816</td>
<td>-0.692663</td>
<td>-0.6927</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.099346</td>
<td>0.100175</td>
<td>0.100282</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.100388</td>
<td>0.100226</td>
<td>0.100232</td>
<td>0.100</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-1)</td>
<td>0.246709</td>
<td>0.247586</td>
<td>0.247650</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.243698</td>
<td>0.246943</td>
<td>0.247230</td>
<td>0.247</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>0.125807</td>
<td>0.125462</td>
<td>0.125597</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.125436</td>
<td>0.125584</td>
<td>0.125595</td>
<td>0.1256</td>
</tr>
<tr>
<td>$Q_{22}$</td>
<td>(0)</td>
<td>1.11994</td>
<td>1.05943</td>
<td>1.02090</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.959916</td>
<td>0.98942</td>
<td>0.991007</td>
<td>0.9919</td>
</tr>
<tr>
<td>$a^a$</td>
<td></td>
<td>0.015040</td>
<td>0.000981</td>
<td>0.000355</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ These values do not include $R_{44}$, for which $a = 0.128122$, 0.012754, and 0.004486.
Table XXIV.C.

Singlet L = 3 results at \( E = 2.25 \).

<table>
<thead>
<tr>
<th>matrix element</th>
<th>( R_N )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁₁ (-1)</td>
<td>-1.649547</td>
<td>-1.276697</td>
<td>-1.276794</td>
<td>0.275</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>-1.6075</td>
<td>2.6664</td>
<td>2.67604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₁₂ (-2)</td>
<td>-1.26475</td>
<td>-1.04455</td>
<td>-1.04455</td>
<td>-1.04455</td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>-0.936464</td>
<td>-0.928150</td>
<td>-0.927782</td>
<td>-0.92</td>
<td></td>
</tr>
<tr>
<td>R₁₃ (0)</td>
<td>-0.561998</td>
<td>-0.564221</td>
<td>-0.564115</td>
<td>0.564</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.468604</td>
<td>-0.46162</td>
<td>-0.465443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₂₂ (0)</td>
<td>-0.46451</td>
<td>-0.464276</td>
<td>-0.464250</td>
<td>0.4641</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.215750</td>
<td>-0.218077</td>
<td>-0.218325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₂₃ (0)</td>
<td>-0.219076</td>
<td>-0.21856</td>
<td>-0.21856</td>
<td>0.2186</td>
<td></td>
</tr>
<tr>
<td>R₂₄ (0)</td>
<td>-0.149667</td>
<td>-0.129856</td>
<td>-0.12617</td>
<td>0.2186</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.111680</td>
<td>-0.118279</td>
<td>-0.118816</td>
<td>-0.1191</td>
<td></td>
</tr>
<tr>
<td>R₃₃ (0)</td>
<td>-0.536305</td>
<td>-0.547924</td>
<td>-0.550189</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.553614</td>
<td>-0.553690</td>
<td>-0.553701</td>
<td>0.5535</td>
<td></td>
</tr>
<tr>
<td>R₄₄ (-1)</td>
<td>-0.988716</td>
<td>-0.978266</td>
<td>-0.973479</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>-0.960838</td>
<td>-0.963619</td>
<td>-0.963797</td>
<td>-0.963</td>
<td></td>
</tr>
<tr>
<td>Q₁₁ (-2)</td>
<td>-0.397504</td>
<td>-0.394269</td>
<td>-0.394810</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>-0.394364</td>
<td>-0.394671</td>
<td>-0.394659</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Q₁₂ (-2)</td>
<td>-0.403341</td>
<td>-0.403187</td>
<td>-0.403745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>-0.396146</td>
<td>-0.403464</td>
<td>-0.403996</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Q₁₃ (-1)</td>
<td>1.000142</td>
<td>0.998492</td>
<td>0.998553</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.998169</td>
<td>0.998753</td>
<td>0.998744</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Q₂₂ (0)</td>
<td>0.724821</td>
<td>0.720958</td>
<td>0.719768</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.719132</td>
<td>0.717908</td>
<td>0.717752</td>
<td>0.7173</td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.014906</td>
<td>0.001539</td>
<td>0.000546</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XXV.

Triplet L = 3, four channel results, calculated in the ls-2s-2p approximation by integration scheme v. For a given matrix element, the first row entries in each column are the values calculated by integration to the indicated $R_N$. The second row entries give the results from the projection procedure applied at that $R_N$. At the bottom of each column are the values of the asymmetry parameter for that projected $k$ matrix. The "BSS" column contains values from Reference 5.
Table XXV.A.

Triplet L = 3 results at \( E = 0.81 \).

<table>
<thead>
<tr>
<th>matrix element</th>
<th>( R^\alpha_N )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} )</td>
<td>(-1)</td>
<td>0.285178</td>
<td>0.286759</td>
<td>0.286704</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.286211</td>
<td>0.286725</td>
<td>0.286673</td>
<td>0.287</td>
</tr>
<tr>
<td>( R_{12} )</td>
<td>(-1)</td>
<td>0.012507</td>
<td>0.075382</td>
<td>0.090419</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.102512</td>
<td>0.110038</td>
<td>0.112365</td>
<td>0.114</td>
</tr>
<tr>
<td>( R_{13} )</td>
<td>(-1)</td>
<td>-0.717827</td>
<td>-0.748651</td>
<td>-0.744803</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.717981</td>
<td>-0.739498</td>
<td>-0.740592</td>
<td>-0.742</td>
</tr>
<tr>
<td>( R_{14} )</td>
<td>(-1)</td>
<td>0.131218</td>
<td>0.137395</td>
<td>0.143594</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.157041</td>
<td>0.148406</td>
<td>0.148182</td>
<td>0.148</td>
</tr>
<tr>
<td>( R_{22} )</td>
<td>(0)</td>
<td>0.072102</td>
<td>0.112980</td>
<td>0.120694</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.127535</td>
<td>0.139304</td>
<td>0.135027</td>
<td>0.1314</td>
</tr>
<tr>
<td>( R_{23} )</td>
<td>(0)</td>
<td>0.593807</td>
<td>0.545991</td>
<td>0.526675</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.485179</td>
<td>0.490078</td>
<td>0.489717</td>
<td>0.4895</td>
</tr>
<tr>
<td>( R_{24} )</td>
<td>(0)</td>
<td>-0.602283</td>
<td>-0.582352</td>
<td>-0.564580</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.359418</td>
<td>-0.508429</td>
<td>-0.523000</td>
<td>-0.5315</td>
</tr>
<tr>
<td>( R_{33} )</td>
<td>(+1)</td>
<td>0.096850</td>
<td>0.118655</td>
<td>0.121834</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.122435</td>
<td>0.125806</td>
<td>0.125950</td>
<td>0.12602</td>
</tr>
<tr>
<td>( R_{34} )</td>
<td>(0)</td>
<td>-0.090376</td>
<td>-0.107020</td>
<td>-0.106687</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.118346</td>
<td>-0.106876</td>
<td>-0.106050</td>
<td>-0.1056</td>
</tr>
<tr>
<td>( R_{44} )</td>
<td>(0)</td>
<td>-0.965562</td>
<td>-0.485190</td>
<td>-0.524331</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.519361</td>
<td>-0.578660</td>
<td>-0.577580</td>
<td>-0.5763</td>
</tr>
<tr>
<td>( Q_{11} )</td>
<td>(-1)</td>
<td>0.186047</td>
<td>1.86303</td>
<td>1.86548</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.186437</td>
<td>0.186506</td>
<td>0.186490</td>
<td>0.187</td>
</tr>
<tr>
<td>( Q_{12} )</td>
<td>(-1)</td>
<td>0.148265</td>
<td>0.166128</td>
<td>0.169296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.163949</td>
<td>0.172555</td>
<td>0.173836</td>
<td>0.175</td>
</tr>
<tr>
<td>( Q_{13} )</td>
<td>(-1)</td>
<td>0.506098</td>
<td>0.515931</td>
<td>0.507927</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.475834</td>
<td>0.500014</td>
<td>0.502340</td>
<td>0.505</td>
</tr>
<tr>
<td>( Q_{14} )</td>
<td>(+2)</td>
<td>0.385298</td>
<td>0.273088</td>
<td>0.244726</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+2)</td>
<td>0.083500</td>
<td>1.86082</td>
<td>0.197355</td>
<td>0.20372</td>
</tr>
<tr>
<td>( \alpha^a )</td>
<td></td>
<td>0.164086</td>
<td>0.021932</td>
<td>0.007636</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) These values do not include \( R_{44} \), for which \( \alpha = 5.07002, 0.110214 \), and 0.035655.
Table XXVIII.

Triplet $L = 3$ results at $E = 1.00$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.369137</td>
<td>.370640</td>
<td>.370537</td>
</tr>
<tr>
<td>(-1)</td>
<td>.370434</td>
<td>.370542</td>
<td>.370483</td>
</tr>
<tr>
<td>$R_{12}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.082514</td>
<td>.146494</td>
<td>.159464</td>
</tr>
<tr>
<td>(-1)</td>
<td>.174885</td>
<td>.179042</td>
<td>.179629</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.144232</td>
<td>-.144809</td>
<td>-.144480</td>
</tr>
<tr>
<td>(0)</td>
<td>-.143733</td>
<td>-.144125</td>
<td>-.144142</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.320117</td>
<td>.327730</td>
<td>.331395</td>
</tr>
<tr>
<td>(-1)</td>
<td>.337715</td>
<td>.335176</td>
<td>.334912</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.418008</td>
<td>.445172</td>
<td>.448886</td>
</tr>
<tr>
<td>(0)</td>
<td>.451610</td>
<td>.454231</td>
<td>.453910</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.228176</td>
<td>.210301</td>
<td>.205076</td>
</tr>
<tr>
<td>(0)</td>
<td>.198220</td>
<td>.195967</td>
<td>.195701</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.371680</td>
<td>-.302142</td>
<td>-.286791</td>
</tr>
<tr>
<td>(0)</td>
<td>-.215987</td>
<td>-.257139</td>
<td>-.260397</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+1)</td>
<td>.123050</td>
<td>.126214</td>
<td>.126809</td>
</tr>
<tr>
<td>(+1)</td>
<td>.127399</td>
<td>.121587</td>
<td>.127607</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.253291</td>
<td>-.265373</td>
<td>-.266654</td>
</tr>
<tr>
<td>(0)</td>
<td>-.268829</td>
<td>-.268097</td>
<td>-.267908</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-.349543</td>
<td>-.405056</td>
<td>-.414523</td>
</tr>
<tr>
<td>(0)</td>
<td>-.430925</td>
<td>-.427837</td>
<td>-.427431</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.167655</td>
<td>.168358</td>
<td>.168451</td>
</tr>
<tr>
<td>(-1)</td>
<td>.167959</td>
<td>.168380</td>
<td>.168364</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>.157640</td>
<td>.192287</td>
<td>.198407</td>
</tr>
<tr>
<td>(-1)</td>
<td>.199790</td>
<td>.206711</td>
<td>.207496</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>.169931</td>
<td>.169170</td>
<td>.168230</td>
</tr>
<tr>
<td>(0)</td>
<td>.166744</td>
<td>.167208</td>
<td>.167217</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+2)</td>
<td>.110697</td>
<td>.123793</td>
<td>.126062</td>
</tr>
<tr>
<td>(+2)</td>
<td>.127975</td>
<td>.129593</td>
<td>.129492</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.083040</td>
<td>.008008</td>
<td>.002807</td>
</tr>
</tbody>
</table>
Table XXV.C.

Triplet $L = 3$ results at $E = 1.44$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>( R_n )</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{11} )</td>
<td>(-1)</td>
<td>0.420318</td>
<td>0.422241</td>
<td>0.422415</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.422201</td>
<td>0.422296</td>
<td>0.422322</td>
<td>0.422</td>
</tr>
<tr>
<td>( R_{12} )</td>
<td>(-1)</td>
<td>-0.235266</td>
<td>-0.185919</td>
<td>-0.175697</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.160169</td>
<td>-0.160074</td>
<td>-0.160138</td>
<td>-0.160</td>
</tr>
<tr>
<td>( R_{13} )</td>
<td>(0)</td>
<td>-0.153026</td>
<td>-0.153692</td>
<td>-0.153962</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.153894</td>
<td>-0.154114</td>
<td>-0.154136</td>
<td>-0.1541</td>
</tr>
<tr>
<td>( R_{14} )</td>
<td>(-1)</td>
<td>0.189532</td>
<td>0.190054</td>
<td>0.187801</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.189404</td>
<td>0.185255</td>
<td>0.185322</td>
<td>0.185</td>
</tr>
<tr>
<td>( R_{22} )</td>
<td>(0)</td>
<td>0.502772</td>
<td>0.502502</td>
<td>0.501962</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.500603</td>
<td>0.500957</td>
<td>0.500905</td>
<td>0.5008</td>
</tr>
<tr>
<td>( R_{23} )</td>
<td>(0)</td>
<td>0.216648</td>
<td>0.212130</td>
<td>0.210689</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.209297</td>
<td>0.208358</td>
<td>0.208262</td>
<td>0.2081</td>
</tr>
<tr>
<td>( R_{24} )</td>
<td>(0)</td>
<td>-0.185283</td>
<td>-0.152111</td>
<td>-0.144850</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.117124</td>
<td>-0.131823</td>
<td>-0.133016</td>
<td>-0.1336</td>
</tr>
<tr>
<td>( R_{33} )</td>
<td>(0)</td>
<td>0.895108</td>
<td>0.911936</td>
<td>0.915296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.919934</td>
<td>0.920233</td>
<td>0.920272</td>
<td>0.9202</td>
</tr>
<tr>
<td>( R_{34} )</td>
<td>(0)</td>
<td>-0.168776</td>
<td>-0.169711</td>
<td>-0.168584</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.167321</td>
<td>-0.167512</td>
<td>-0.167510</td>
<td>-0.1675</td>
</tr>
<tr>
<td>( R_{44} )</td>
<td>(0)</td>
<td>-0.167141</td>
<td>-0.185543</td>
<td>-0.186345</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.191994</td>
<td>-0.190457</td>
<td>-0.190302</td>
<td>-0.1901</td>
</tr>
<tr>
<td>( Q_{11} )</td>
<td>(-1)</td>
<td>0.151732</td>
<td>0.153351</td>
<td>0.153415</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.153207</td>
<td>0.153333</td>
<td>0.153349</td>
<td>0.153</td>
</tr>
<tr>
<td>( Q_{12} )</td>
<td>(-2)</td>
<td>0.429460</td>
<td>0.377531</td>
<td>0.369511</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.355432</td>
<td>0.358580</td>
<td>0.358974</td>
<td>0.36</td>
</tr>
<tr>
<td>( Q_{13} )</td>
<td>(0)</td>
<td>0.173659</td>
<td>0.173721</td>
<td>0.174055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.173795</td>
<td>0.174057</td>
<td>0.174091</td>
<td>0.1740</td>
</tr>
<tr>
<td>( Q_{14} )</td>
<td>(+1)</td>
<td>0.525403</td>
<td>0.533900</td>
<td>0.535020</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.538010</td>
<td>0.536717</td>
<td>0.536467</td>
<td>0.53636</td>
</tr>
<tr>
<td>( \alpha )</td>
<td></td>
<td>0.030680</td>
<td>0.003342</td>
<td>0.001194</td>
<td></td>
</tr>
</tbody>
</table>
Table XXV.D.

Triplet $L = 3$ results at $E = 2.25$.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>PSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$</td>
<td>(-1)</td>
<td>0.482606</td>
<td>0.480627</td>
<td>0.480966</td>
<td>0.479</td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.480836</td>
<td>0.480870</td>
<td>0.480833</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$</td>
<td>(-1)</td>
<td>-0.443956</td>
<td>-0.412189</td>
<td>-0.405742</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.394966</td>
<td>-0.395713</td>
<td>-0.395795</td>
<td>-0.396</td>
</tr>
<tr>
<td>$R_{13}$</td>
<td>(0)</td>
<td>-0.138832</td>
<td>-0.139615</td>
<td>-0.139900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.140089</td>
<td>-0.140192</td>
<td>-0.140202</td>
<td>-0.1402</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>(-1)</td>
<td>0.154284</td>
<td>0.140952</td>
<td>0.138768</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.132175</td>
<td>0.134965</td>
<td>0.134955</td>
<td>0.133</td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>(0)</td>
<td>0.515427</td>
<td>0.512859</td>
<td>0.512175</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.510949</td>
<td>0.511069</td>
<td>0.511059</td>
<td>0.5109</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>(0)</td>
<td>0.165486</td>
<td>0.164748</td>
<td>0.164374</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.164154</td>
<td>0.163764</td>
<td>0.163731</td>
<td>0.1637</td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>(-1)</td>
<td>-1.03189</td>
<td>-0.866437</td>
<td>-0.830582</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>-0.702402</td>
<td>-0.766982</td>
<td>-0.772188</td>
<td>-0.774</td>
</tr>
<tr>
<td>$R_{33}$</td>
<td>(0)</td>
<td>0.734658</td>
<td>0.743508</td>
<td>0.745226</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.747814</td>
<td>0.747855</td>
<td>0.747865</td>
<td>0.7476</td>
</tr>
<tr>
<td>$R_{34}$</td>
<td>(0)</td>
<td>-0.125931</td>
<td>-0.125551</td>
<td>-0.125186</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>-0.124188</td>
<td>-0.124398</td>
<td>-0.124399</td>
<td>-0.1245</td>
</tr>
<tr>
<td>$R_{44}$</td>
<td>(-2)</td>
<td>1.65803</td>
<td>0.997939</td>
<td>0.887173</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.659715</td>
<td>0.725826</td>
<td>0.731267</td>
<td>0.74</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>(-1)</td>
<td>0.144582</td>
<td>0.143397</td>
<td>0.143584</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-1)</td>
<td>0.143567</td>
<td>0.143529</td>
<td>0.143535</td>
<td>0.143</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>(-2)</td>
<td>0.892855</td>
<td>0.761582</td>
<td>0.736721</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-2)</td>
<td>0.699858</td>
<td>0.699664</td>
<td>0.699716</td>
<td>0.70</td>
</tr>
<tr>
<td>$Q_{13}$</td>
<td>(0)</td>
<td>0.106408</td>
<td>0.107059</td>
<td>0.107408</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td>0.107582</td>
<td>0.107730</td>
<td>0.107744</td>
<td>0.1077</td>
</tr>
<tr>
<td>$Q_{14}$</td>
<td>(+1)</td>
<td>0.267996</td>
<td>0.267584</td>
<td>0.267397</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(+1)</td>
<td>0.267438</td>
<td>0.267118</td>
<td>0.267074</td>
<td>0.26697</td>
</tr>
</tbody>
</table>

$\alpha \quad 0.019853 \quad 0.001945 \quad 0.000704$
Table XXVI.

Singlet $L = 4$ results at $E = 1.44$.

For explanation, see caption to Table XXV.

<table>
<thead>
<tr>
<th>matrix element</th>
<th>$R_N$</th>
<th>40</th>
<th>120</th>
<th>200</th>
<th>BSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{11}$ (-1)</td>
<td>0.207390</td>
<td>0.208227</td>
<td>0.208358</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.208819</td>
<td>0.208311</td>
<td>0.208314</td>
<td>0.208</td>
<td></td>
</tr>
<tr>
<td>$R_{12}$ (-2)</td>
<td>0.181283</td>
<td>0.488692</td>
<td>0.551599</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.724915</td>
<td>0.656166</td>
<td>0.650573</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$ (0)</td>
<td>-0.107445</td>
<td>-0.107097</td>
<td>-0.107191</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.106867</td>
<td>-0.107063</td>
<td>-0.107209</td>
<td>-0.1071</td>
<td></td>
</tr>
<tr>
<td>$R_{14}$ (-1)</td>
<td>0.228920</td>
<td>0.238012</td>
<td>0.237691</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.236548</td>
<td>0.238337</td>
<td>0.238441</td>
<td>0.239</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$ (0)</td>
<td>0.115171</td>
<td>0.124099</td>
<td>0.125610</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.129082</td>
<td>0.127867</td>
<td>0.127755</td>
<td>0.1276</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$ (0)</td>
<td>0.389983</td>
<td>0.387065</td>
<td>0.385821</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.373826</td>
<td>0.382453</td>
<td>0.383152</td>
<td>0.3835</td>
<td></td>
</tr>
<tr>
<td>$R_{24}$ (0)</td>
<td>-0.442711</td>
<td>-0.426678</td>
<td>-0.422490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.427520</td>
<td>-0.416483</td>
<td>-0.415860</td>
<td>-0.4156</td>
<td></td>
</tr>
<tr>
<td>$R_{33}$ (0)</td>
<td>0.230579</td>
<td>0.261455</td>
<td>0.267669</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.279702</td>
<td>0.277406</td>
<td>0.277105</td>
<td>0.2769</td>
<td></td>
</tr>
<tr>
<td>$R_{34}$ (-1)</td>
<td>0.613978</td>
<td>0.588430</td>
<td>0.587169</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.586987</td>
<td>0.588300</td>
<td>0.588191</td>
<td>0.588</td>
<td></td>
</tr>
<tr>
<td>$R_{44}$ (0)</td>
<td>-0.398824</td>
<td>-0.414548</td>
<td>-0.449487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>-0.471320</td>
<td>-0.462243</td>
<td>-0.461420</td>
<td>-0.4610</td>
<td></td>
</tr>
<tr>
<td>$Q_{11}$ (-2)</td>
<td>0.283174</td>
<td>0.284993</td>
<td>0.285360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.286505</td>
<td>0.285182</td>
<td>0.285213</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>$Q_{12}$ (-2)</td>
<td>0.813163</td>
<td>0.816591</td>
<td>0.816690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>0.770382</td>
<td>0.810382</td>
<td>0.813691</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>$Q_{13}$ (-1)</td>
<td>0.511039</td>
<td>0.507072</td>
<td>0.508302</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>0.512873</td>
<td>0.508520</td>
<td>0.508314</td>
<td>0.508</td>
<td></td>
</tr>
<tr>
<td>$Q_{14}$ (0)</td>
<td>0.921944</td>
<td>0.866437</td>
<td>0.851238</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>0.837571</td>
<td>0.826200</td>
<td>0.826042</td>
<td>0.8261</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha$ | 0.056122 | 0.005981 | 0.002123 |     |     |