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Technical Report

SLOW-NEUTRON SCATTERING AND THE ROTATIONAL DYNAMICS OF MOLECULES

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ABSTRACT

Quantum descriptions of slow-neutron inelastic scattering cross sections which are sensitive to the presence of internal rotational degrees of freedom in molecules are presented. The details of rotational line shape as affected by the formation and decay of locally ordered structures in polar diatomic liquids are also discussed. A careful review is made of rotational Hamiltonians which include internal rotation for various classes of molecules possessing a threefold internal barrier. Rotational wave functions are derived and examined in the general case. High and low internal-barrier approximations suitable for the description of neutron scattering are found for symmetric molecules which are either freely rotating or whose over-all rotations are hindered. New cross section formulae for the scattering by molecular rotational degrees of freedom are obtained using a suitable expansion of the neutron operators. In the free over-all rotation case a quasi-classical approximation is attempted and comparison made with experimental data for ethane and dimethyl acetylene. Hindrance of the over-all rotational motion is treated by means of a strong coupling between the permanent electric dipole moment of the molecule and a local electric field which represents the orientation-dependent effects of intermolecular forces and hydrogen bonding. Calculations are compared with experiment for liquid methanol at two angles. The general quantum line shape formulation of slow-neutron scattering based on the damping theory is reviewed and analysis made of the effect of a position-, orientation-dependent perturbation on the line shape of a hindered rotational line of a polar diatomic liquid. The width function is a measure of the lifetime of the initial state and hence of the local structure in the liquid.

CHAPTER I

INTRODUCTION

> "...the whole burden of science seems to consist in this, from the phenomena of motions to investigate the forces of nature, and from these forces to demonstrate the other phenomena."
>
> ---I. Newton (1686)

SYNOPSIS

This dissertation presents a quantum description of inelastic neutron scattering as it reveals the rotational dynamics of molecules in a given state of matter. Original contributions relate to the description of the effects of internal rotational degrees of freedom of molecules on neutron scattering and to the calculation of rotational neutron line shapes. The new results are compared with experimental measurements wherever possible.

1.1 THE PROBLEM IN PERSPECTIVE

Our environment of matter, composed of elements and their chemical compounds, may exist in three different physical states, depending on their temperature and pressure. These states are called, respectively, the solid, liquid, and gaseous states. Generally speaking, the solid state is stable at low temperatures and/or high pressures; the liquid state is stable in an intermediate range of temperatures and pressures; and the gaseous state is stable at high temperatures and low pressures.

On the macroscopic level the solid state is generally characterized by high cohesion and rigidity; the liquid state by high cohesion, comparative lack of rigidity and low resistance to flow; and the gaseous state by low cohesion, lack of rigidity, and very low resistance to flow. On the molecular level the solid state may exhibit a rather regular crystalline structure and the gaseous state complete molecular disorder, while the liquid state is, in some sense, intermediate between these extremes.

The above statements are among the oldest and most basic facts of physical science, yet they still present a considerable challenge to man's ingenuity.

It would seem that, given the proper understanding, it ought to be possible to describe the existence and differences of these three states of matter in terms of their microscopic structure and the properties of the molecules, atoms, or ions of which they are built. Indeed, a large part of modern physics is concerned with the relations between the physical behavior of a composite system and that of its constituent parts. Moreover, with sufficient knowledge of the properties of these basic constituents, it ought to be possible to make quantitative predictions of the detailed properties of the solid, liquid, and gas. This ability to predict is of fundamental importance to the scientist and technologist no matter what his field. Following from the above statements, the most general objective of this dissertation is to contribute to the understanding of our environment by a theoretical study of some of the dynamical properties of molecules in a given state of matter.

In order to study the properties of the atoms and molecules which make up some arbitrary macroscopic aggregation, in one of the three physical states, an appropriate tool is needed. Such a tool for use in determining the molecular dynamics in macroscopic systems is not easily found. However, since the advent of nuclear reactors in the 1940's with their attendant high neutron fluxes, the scattering of slow neutrons has provided a suitable tool for systems in any physical state. The neutron has a mass roughly of the order of atomic masses, and hence a slow neutron of energy .01 to .1 ev, in collision with a system of atoms and molecules, has a reasonable chance of picking up or losing quanta of any of the characteristic energies of the system. The changes in energy of the scattered neutrons are relatively large and easily measurable. At the same time, since the de Broglie wavelength of a slow neutron is of the order of atomic separations, the neutron is sensitive to the symmetries of the system and responds to all kinds of motions in the system, at least those which manifest themselves in the "interaction time" of the neutrons.

Any analysis of slow neutron scattering requires not only an understanding of the properties of neutrons and the spectrometers used in experimental studies, but also, knowledge of some of the basic molecular physics involved in describing the complex motions molecules may undergo. Of the various modes of molecular motions, translations of the center-of-mass and rotations of the molecules are of particular interest because of their more sensitive dependence upon the physical state of the system. The characteristic energies associated with these motions are of the order of .001 to .1 ev, the same order as an incident slow neutron, and hence measurements of energy distributions of the inelastically scattered neutrons provide a method of directly studying the details of molecular translations and rotations, and the influences of the surroundings on these motions. In this respect, slow neutrons are very suitable microscopic probes for the investigation of intermolecular forces. Thus, a more specific objective of this dissertation is to study the effects of the forces between molecules comprising a substance in a given physical state, with particular interest in the liquid state.

The least understood state is the liquid state. If there were no other reasons than that, an investigation of liquids would be interesting. But other reasons do exist and for a nuclear engineer a knowledge of the liquid state can be applied to predictions of the shape of neutron spectra and the detailed description of neutron thermalization, so that a study of liquids becomes a practical activity. Indeed, it is an activity with a great economic incentive, since obtaining reliable reactor-physics answers from experiment is slow and the design of sufficient flexibility into the final power reactor, so as to allow for large uncertainties in the neutronic behavior, usually entails prohibitive expense.

It has been customary to classify liquids into two classes called normal liquids and associated liquids according to certain empirical rules, but the rules for such a classification cannot be rigidly defined. A liquid will usually be normal if the internal degrees of freedom of each molecule are not seriously disturbed by the close proximity of the liquid. Internal degrees of freedom involve vibrational, rotational, and electronic motions. In an associated liquid the molecules interact so intimately that the internal degrees of freedom are seriously modified from those present in a molecule of the gas. Clearly, a normal liquid is a simpler system and an understanding of its properties is an important step toward the understanding of liquids in general. The most obvious examples of normal liquids are the noble gases in their condensed state.

But even if association were to be momentarily excluded from consideration, there are incomparably greater difficulties in applying the available scientific and mathematical tools to a liquid than to a dilute gas or to a crystal. For in a dilute gas there is almost complete randomness of configuration and in a crystal there is almost complete order; but in a liquid there is neither and it is this fact which makes it so difficult to find a useful description.

However, there is another important reason why the molecular theory of the liquid state is very much more difficult than that of the gaseous or solid state and it is one that is sometimes overlooked. This reason is that despite the presence of some regularities which are generally inherent in all liquid systems, complexities of macroscopic physical behavior as exist in liquids correspond very closely to complexities of molecular dynamics and structure between various narrow classes of liquids. A superficial comparison shows that there is no parallel for liquids of the gas laws, or Debye's approximation for the specific heat of solids. Some liquids obey Andrade's law of viscosity precisely, while others deviate from it very widely. There is no simple way of representing the coefficient of thermal conduction of any wide class of liquids. Thus, a study of "liquids in general" is not likely to be very informative. Indeed, regularities of behavior will be found only within groups of liquids with similar molecular constitution such that the molecular dynamics are similar.

Many kinds of molecules possess permanent electric (or magnetic) moments, which are dipole, quadrupole, or higher multipole in character. The force between two such molecules depends on their mutual orientation as well as the distance between them so that the idea of central forces is inapplicable. A polar liquid is composed of molecules possessing a permanent moment which is largely independent of the presence of other molecules. In a liquid the structure of a molecule may be deformed to some extent by its neighbors, and its electric moments are therefore subject to fluctuations; but, in a polar liquid, these should be secondary to the average "permanent" moments of the molecule. Much depends on whether the polarity is localized in certain regions near the "surface" of the molecule, or whether it is approximately concentric with the center of mass. With localized polarity, bonds are formed between regions of different molecules with opposite polarity. These bonds are, in the liquid, constantly broken and reformed, as a result of thermal agitation. It is important to notice that the formation of polar bonds of this type does not completely fix the mutual orientation of the molecules, since certain bond "bending" can occur.

Chemical bonding, arising through the presence of unpaired electrons on the molecules, may be responsible for a somewhat different type of intermolecular force from that found in polar liquids. The chemical bond is thought of as capable of saturation, and once formed between two molecules is no longer effective in binding other molecules. The attraction between two ions of opposite charge has a similar property, and is regarded as a special type of chemical bond. The forces between dipolar molecules, where the polarity is localized in certain regions near the "surface" of each molecule, are also similar, and so these polar liquids are regarded as associated liquids. It is essential that the energy of the chemical bond in the associated liquid is not greater than the fluctuations in the thermal energy, or otherwise the association would be permanent.

The nature of the association resulting from unpaired electrons on a molecule depends on the number of such unpaired electrons. When there is only one, the molecules merely associate in pairs. When there are two, the molecules may associate in chains or rings. When there are more than two, very complicated branching linkages such as are found in the glasses are possible.

As might be expected, the special structure of polar and associated liquids is reflected in the dynamical motions molecules may undergo and in the physical properties of the liquids. Translations and rotations of the molecules may be hindered by the intermolecular forces. The viscosity, surface tension, and vapor pressure or volatility of a liquid are good indices of the degree of association. It is not hard to understand in a qualitative way the connection between the molecular configuration and dynamics, and these macroscopic properties. However, quantitatively little has been achieved to estimate or predict them.

Theories of the liquid state fall into two broad classes, neither of which has had startling success even with the simple monatomic liquids. The one class of theories starts from a description of the structure, usually a simplified and approximate description, and leaves the question of how the structure is determined by the molecular properties to be answered after the fact. Theories of this class are called "lattice" theories because the proposed structure often bears some relation to the regular lattice structure of a crystalline solid. Theories of the other class are concerned with the process by which the intermolecular forces determine the structure, since a correct description of this process should lead, in principle, to a correct description of the actual structure. Theories of this class are called "distribution function" theories because their formulations of the problem involve distribution functions which specify the probability of finding sets of molecules in particular configurations. Both classes of theories have respectable antecedents. The lattice theories develop logically from successful methods in the theory of solids, while distribution function theories develop ideas found to some extent in the kinetic theory of gases.

However, most of the older theories, which are briefly reviewed in Appendix C, are largely equilibrium theories which use the methods of equilibrium statistical mechanics so that the dynamics of the system of molecules is not a predominant consideration. According to statistical mechanics the equilibrium properties may be calculated by averaging with an appropriate weighting factor over all accessible configurations of the molecules. The purpose of a model or ideal structure in statistical mechanics is simply to provide a convenient classification of the actual configurations available to the molecules, in order to make the required averaging possible. In fact, starting from a given model or ideal structure, it is usually possible to develop a formal sequence of mathematical approximations, the results of which should ultimately converge to the correct equilibrium results for the liquid. In practice, the detailed evaluation of these approximations rapidly becomes prohibitively difficult, so that to obtain a workable theory it is essential to choose a model or ideal structure which is already as close as possible to the real structure of the liquid.

It is clear that the word "structure" has different implications for liquids than it does for solids. Very generally speaking, a solid has a single, nearly static crystal structure which is only slightly blurred by the thermal motions of the molecules, but in a liquid the instantaneous structure changes continually and grossly because of the random thermal motions. This is underlined by the experimental fact that diffusion in solids is very slow, but in liquids diffusion is much more rapid.

Thus, it appears that by studying the dynamics of a system of molecules in the liquid state, a proper understanding of the accessible configurations and their relative probabilities may be achieved and hence lead to a correct theory of liquids. Since dynamics consists of kinematics, the description of the motion of molecules without reference to the causes of the motion, and of kinetics, the description of the relationship between the mutual influences and the resulting motions, not only the motions are studied, but also the intermolecular forces can be investigated.

The experimental evidence concerning the properties of liquids falls into four classes: (i) direct structural evidence on molecular arrangements from x-ray and neutron angular distributions in the form of radial distribution functions, (ii) thermodynamic evidence from measurement of equilibrium properties, (iii) evidence from measurements of nonequilibrium properties such as viscosity, thermal conductivity, and diffusion coefficients, and (iv) evidence on liquid molecular dynamics from such sources as neutron and photon energy distributions, microwave and infrared absorption measurements, ultrasonic experiments, dielectric relaxation measurements, and nuclear magnetic resonance measurements. No theory could be considered completely explored until compared with all four classes of evidence, but the most fruitful line of investigation may reside with the fourth class, and scattered neutron energy distributions particularly may prove to be valuable due to the absence of selection rules. Thus, we have indicated the reasons for attempting to contribute something fundamental to the theory of inelastic neutron scattering and have established the logical point of contact between neutron scattering measurements and various other modern techniques.

However, we will see that due to an experimental limitation in resolution the translational degrees of freedom of molecules are not as directly accessible to measurement by neutron scattering as are certain rotational transitions, and hence it is appropriate to focus here upon the rotational dynamics of molecules, and attempt to effect some kind of separation which will allow investigation of this one aspect of the total problem.

In particular, two problem areas in which original contributions may prove to be worthwhile are those of the description of the effects of internal rotational degrees of freedom of molecules on neutron scattering and to the calculation of rotational neutron line shape as affected by the formation and decay of locally ordered structures in polar diatomic liquids. Internal rotation refers to the rotation of one part of a molecule relative to the rest of the molecule.

Now having indicated the connection between the limited problem specifically addressed in this dissertation and the nearly limitless problems offered by a study of liquids, we proceed to comment briefly on those aspects of the philosophy of theoretical work in physics upon which understanding of the subject depends and from which this investigation has received its direction. A proper perspective is then achieved.

In general, theory is necessary in order to carry out and correctly interpret meaningful experiments. Every theory is phenomenological to some degree. That is to say, every theory requires certain quantities which are not determinable by it within its domain of validity and which must be supplied to the theory on the basis of appropriate measurements. We may define a theory as a limited, axiomatic, deductive, logical-mathematical system and observe that there exist several levels of theory, one being the covering theory of the next lower one. A covering theory simply is a more general theory with a greater domain of validity than the theory which it covers. Progress in theoretical physics then, involves the construction of an all-inclusive theory which is phenomenologically minimal, but progress is also attained when knowledge results from new applications of an existing theory. It is this latter area in which this dissertation makes its contributions, namely, the use of quantum theory in new descriptions of phenomena.

Any student of science must struggle to grasp new relations and new notions, and the simple expedient of concrete mechanical visulazation is an obvious course of procedure in this struggle. With more maturity in the study of physics, or with a clear understanding of a new phenomenon as it is visualized, a more complete and correct formulation in some general scheme of nature may be possible, even necessary, because of the failure of the mechanical analogy in its details. At any rate, in the process of achieving the ultimate goal of a scientific theory (which I believe is to demonstrate the logical necessity of the behavior of the physical world from as simple a set of basic assumptions as possible), the stimulus of mechanical visualization will have played its role. It seems to be the very fallibility of such mechanical pictures which makes experimental test imperative and hence leads to further investigations and clearer knowledge. This is particularly true when mathematical models, such as will be employed in the present work, are used. Refinements in the underlying ideas and hence the models would certainly be necessary if much more sensitive measurements indicated their need.

1.2 OUTLINE OF THIS STUDY

The specific problems for which original solutions are presented in the present work involve descriptions of slow-neutron scattering which are sensitive to the presence of internal rotational degrees of freedom in molecules and to the formation and decay of locally ordered structures in polar liquids. However, the more general problems of the effects of rotational dynamics, both free and hindered, and of line shape are discussed in some detail.

In Chapter II, the general quantum line shape formulation of slow-neutron scattering for arbitrary macroscopic aggregates based on the damping theory is reviewed, as are the types of measurements with which calculations are to be compared. The limit of zero line width and shift is seen to be the conventional formulation of Zemach and Glauber. Since the validity of some of the assumptions made have since been investigated by Plummer, the formulation is now theoretically on somewhat firmer ground. The connection with the space-time correlation function approach of Van Hove is shown and the scattering law technique is commented upon. The reduction of the line shape formulation to a form which is used in later calculations is also displayed.

Since the addition of an internal rotational degree of freedom complicates the interpretation of experiments, we employ the simpler zero-line-width-and-shift formalism in Chapter III to describe the effects of both free and hindered internal rotation in the presence of free-over-all rotation and translation of a molecule as occurs in gases and some normal liquids. An effective strong coupling of internal rotational transitions to free over-all rotational transitions about the axis of internal rotation is seen as a type of weak rotational selection rule—the presence of one motion may mask the presence of another. A careful analysis of the rotational Hamiltonians which include internal rotation for various classes of molecules is presented. A threefold internal barrier is assumed throughout. The rotational wave functions are derived and examined in the general case. High- and low-barrier approximations suitable for the description of neutron scattering are found for symmetric molecules. New formulae for the scattering by rotational degrees of freedom are obtained. A review of the description of free rotation of rigid rotators is given and the computational difficulty which it presents for symmetric molecules is described. The more practical aspects of group theory are used including 3-j symbols for describing the coupling of angular momenta. A quasi-classical approximation is given and computations are made for ethane and dimethyl acetylene compared with experiment. The influence of this internal rotational degree of freedom on the total cross section is described.

Chapter IV is devoted to the description of the effects of internal rotation in the presence of hindered over-all rotation and translation of a molecule as occurs in polar and associated liquids and extension to problems of the solid state is discussed. The inclusion of both hindered and free axial over-all rotations in the description is approximated by uncoupling them. Numerical computations are given for liquid methanol at two angles and compared with experimental results. Chapters III and IV are believed to constitute a rather complete analysis of the dominant effects of internal rotation on inelastic neutron scattering in the limit of the zero-line-width-and-shift description.

By examining the hindered rotational transitions of linear (diatomic) molecules the complications arising from free axial over-all rotations and internal rotations disappear and the use of the full line shape formalism is practical and informative. In Chapter V the line shape contributions of the width of the levels, which is a direct measure of their lifetime, are employed to investigate the formation and decay of locally ordered structures in diatomic polar liquids. The results of numerical computations are given for liquid hydrogen bromide.

Finally, in Chapter VI the conclusions of this study are presented and suggestions for further work are made.

CHAPTER II

GENERAL LINE SHAPE FORMULATION OF SLOW-NEUTRON SCATTERING BY MACROSCOPIC SYSTEMS

> "Lack of experience diminishes our power of taking a comprehensive view of the admitted facts. Hence, those who dwell in intimate association with nature and its phenomena grow more and more able to formulate, as the foundation of their theories, principles such as to admit of a wide and coherent development; while those whom devotion to abstract discussion has rendered unobservant of the facts are too ready to dogmatize on the basis of a few observations."
>
> Aristotle (354 B.C.)

2.1 INTRODUCTION

We present here a general quantum description of slow-neutron scattering by molecules in an arbitrary macroscopic system, including a description of line shape. A complete, detailed theory of the interaction of neutrons of any energy with individual nuclei is as yet unavailable, and an understanding of this is prerequisite to the development of a complete theory of the interaction with aggregates of nuclei. However, since we are limiting the discussion to slow neutrons, the interaction of neutrons with individual nuclei can be described by a single, experimentally determined parameter, the scattering length, which is defined as the radius at which the zero energy limit of the asymptotic radial wave function vanishes. Although independent of energy, the scattering length is in general a function of the total spin angular momentum of the neutron and the nucleus. The magnetic scattering of neutrons, in which electron scattering is not negligible, will not be discussed since the interaction is basically different.

When slow neutrons are scattered by a system of chemically bound nuclei, the recoiling nuclei are part of the larger system and any transfers of energy and momentum from the neutron to the system must be consistent with its quantum nature. In contrast to earlier formulations, the finite lifetime of various quantum states in the system can be taken into account in the following formalism by ascribing finite widths to their energy levels. The formalism is suitable for the analysis of low-energy inelastic scattering, particularly by solids and liquids, on the basis of specific dynamical models. At the outset, an independent-particle model is assumed to describe the dominant aspects of molecular motion in which molecular translations, rotations, and vibrations are approximated by independent motions so that the effects characteristic of molecular motions may be calculated. The essence of the approach, however, lies in its perturbation treatment of certain "damping" mechanisms which can be kept as part of the dynamical model.

We begin by considering an idealized experiment which illustrates the type of measurements with which subsequent calculations are to be compared. Some of the neutrons in a monoenergetic beam impinging upon a scattering sample which collide with target molecules are deflected from the beam with energies greater or less than they had before scattering. By counting neutrons having a given energy scattered in a given direction, an energy distribution is obtained. If neutrons regardless of energy are counted at a series of different scattering angles, an angular distribution is obtained. Or, in a total scattering measurement all scattered neutrons are counted regardless of their directions or energies and the result is a function of incident neutron energy only. Of these three types of measurement, the energy distribution experiment is clearly the most fundamental, in terms of information about the scattering process, since the others are integral measurements in relation to it. In this idealized case, the scattering event under consideration is treated as a single collision process, and the resolution of the neutron detector is taken to be infinitely sharp. However, in practical applications these conditions are not strictly met, since the thickness of the sample is limited by multiple scattering and since there is an inherent finite resolution associated with any energy-selecting or measuring device which limits the precision with which energies can be specified.

The fundamental quantity which characterizes the interaction in the energy distribution measurement is the probability that an incident neutron with initial energy E_i will be scattered into direction $\underline{\Omega}$ with final energy E_f. When normalized to unit scatterer, this probability is called the energy and angular differential cross section. We define $d^2\sigma/d\Omega dE_f$ $d\Omega dE_f$ to be the number of neutrons scattered into an element of solid angle $d\Omega$ about $\underline{\Omega}$, where $\underline{\Omega} = \underline{k}_f/k_f$, having energy in dE_f about $E_f = \hbar^2 k_f^2/2m$ per second per atom of scatterer divided by the number of incident neutrons of initial energy E_i per square centimeter per second. Alternatively, $d^2\sigma/d\Omega dE_f$ is the time rate of change due to scattering in the expected number of neutrons having momentum in $\hbar^3 d^3 k_f$ about $\hbar \underline{k}_f$ given that initially they had momentum $\hbar \underline{k}_i$, divided by the initial neutron current and the number of atoms in the scattering sample.

2.2 THE DIFFERENTIAL CROSS SECTION

In order to derive an expression for $d^2\sigma/d\Omega dE_f$ we first note that the expected number of neutrons having a momentum $\hbar \underline{k}_f$ and spin τ_f in our system of a neutron beam and scattering sample is given by

$$\chi(\underline{k}_f, \tau_f) = \mathrm{Tr}\left[\rho(\underline{k}_f, \tau_f) D\right], \tag{2.1}$$

where ρ is the number operator for neutrons of the specified kind, and D is the usual density operator of the system. The Hamiltonian H of the system of this experiment is

$$H = \frac{p^2}{2m} + H^s + V^n, \tag{2.2}$$

where the interaction between neutrons has been neglected, and $p^2/2m$ is the kinetic energy of the neutrons, H^s is the Hamiltonian of the scattering system, and V^n is the interaction potential between the neutrons and the scatterer.

The Hamiltonian H^s represents only the various molecular energies of the scattering system. Since the neutron energies are much too low to excite any electronic levels and electron scattering is negligible, the electronic energies are of no interest and hence, the Born-Oppenheimer approximation[1] has been invoked. However, for any real physical system of interest the eigenfunctions of the Hamiltonian H^s are not available, although they are available for a part of H^s. That is, the eigenvalue problem

$$(\mathcal{H}^s - E_n^s)|n\rangle = 0, \tag{2.3}$$

can be solved, where $\mathcal{H}^s$ is a part of H^s, namely,

$$H^s = \mathcal{H}^s + H'. \tag{2.4}$$

In order to explain the dominant aspects of certain scattering experiments H' is usually ignored completely. However, interpretation of the details of recent neutron scattering experiments requires a more complete analysis than can be obtained by ignoring H'. From the valuable information about the anharmonic forces in crystals which can be gained from a comparison of the experimental and theoretical neutron line shapes, it is anticipated that a study of neutron line shape may also prove to be a powerful tool in the investigation of intermolecular forces in liquids.

Hence, let H^o and V denote the unperturbed Hamiltonian and the perturbation respectively, and let them be

$$\begin{aligned} H^o &= \mathcal{H}^s + \frac{p^2}{2m}, \\ V &= V^n + H'. \end{aligned} \tag{2.5}$$

By computing the trace in (2.1) in a representation where H^o, p, and the projection of the neutron spin are diagonal, the rate of change in the neutron number of a specified kind can be expressed as[2,3]

$$\frac{d}{dt}\chi = \sum_{n_i, n_f} P_{n_i}(\eta_f - \eta_i) W_{n_f n_i}, \tag{2.6}$$

In this expression n_i and n_f label the initial and final states of the system, P_{n_i} and the occupation numbers η_f and η_i are the diagonal elements of the density matrix and the number operator:

$$P_{n_i} \equiv D_{n_i n_i}, \quad \eta_f \equiv \rho_{n_f n_f}, \quad \eta_i \equiv \rho_{n_i n_i},$$

and the transition probability per unit time $W_{n_f n_i}$ is defined as follows

$$W_{n_f n_i} = \frac{1}{t}\left|\langle n_f | e^{-iHt/\hbar} | n_i \rangle\right|^2. \tag{2.7}$$

The eigenstates of the system, neutrons plus scatterer, $|n_i\rangle$ and $|n_f\rangle$ are labelled in detail as

$$|n_i\rangle = |\eta_i(\underline{k}, \tau)\rangle |i\rangle,$$
$$|n_f\rangle = |\eta_f(\underline{k}, \tau)\rangle |f\rangle,$$

where $|\tau_f\rangle$ and $|\tau_i\rangle$ denote the spin states of the neutrons, and $|i\rangle$ and $|f\rangle$ are the eigenstates of $\mathcal{H}^s$ including the spin states of the scatterer.

Since the occupation numbers for neutrons are clearly either zero or one, $(\eta_f - \eta_i)$ in (2.6) is either +1 or -1. The terms with positive sign correspond to the scattering of neutrons out of the state $(\underline{k}_f, \tau_f)$. The initial occupation numbers for our idealized experiment with its monoenergetic beam of neutrons, are

$$\eta_i(\underline{k}, \tau) = 1, \quad \text{for } \underline{k} = \underline{k}_i \text{ and } \tau = \tau_i$$
$$= 0, \quad \text{otherwise.}$$

Now the time rate of change due to scattering in the expected number of neutrons having momentum in $\hbar^3 d^3 k_f$ can be seen from (2.6) to be

$$\frac{d}{dt}\int N(\underline{k}_f)\,d^3k_f = \sum_{\underline{k}_f \in d^3k_f} \sum_{i,\tau_i} P_{n_i} \sum_{f,\tau_f} W_{n_f n_i} \,. \qquad (2.8)$$

P_{n_i} may now be approximated by $P_i P_{\tau_i} P_{\underline{k}_i}$ and $P_{\underline{k}_i}$ is unity since the neutrons are completely prepared in the monoenergetic beam. Further, P_{τ_i} can be set equal to 1/2 if the beam is assumed to be unpolarized.

Using these results and dividing by the initial neutron current $\hbar k_i/mL^3$ and the number of atoms N, we arrive at a formal expression for the double differential cross section

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \frac{m^2 L^6}{2N(2\pi\hbar)^3}\,\frac{k_f}{k_i} \sum_{i,f,\tau_i,\tau_f} P_i W_{n_f n_i} \,, \qquad (2.9)$$

where L^3 is the volume of normalization.

If, as is the case in practice, the incident neutrons are not completely prepared, then it is necessary to replace $P_{\underline{k}_i}$ above not by unity but by a distribution normalized to unit area, and hence Equation (2.9) must be averaged over this distribution and becomes

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \frac{m^2 L^6 k_f}{2N(2\pi\hbar)^3} \int K_1(\underline{k}_i, \underline{k}_{i0}) \frac{1}{k_i} \sum_{i,f,\tau_i,\tau_f} P_i W_{n_f n_i}\, d^3k_i \,. \qquad (2.10)$$

The same inherent finite resolution associated with any energy-selecting device which limits the precision with which the incident neutron energies can be prepared also limits the precision with which the final neutron energies can be specified in counting. Therefore, the differential cross section one can measure in a realistic experiment corresponds to further averaging (2.10) over a distribution in $\underline{k}_f$ normalized to unit area, and hence finally

$$\frac{d^2\sigma}{d\Omega_i dE_f}=\frac{m^2L^6}{2N(2\pi\hbar)^3}\int K_2(\underline{k}_f,\underline{k}_{f0})\int K_1(\underline{k}_i,\underline{k}_{i0})\frac{k_f}{k_i}\sum_{i,f,z_i,z_f}P_i W_{n_f n_i}\,d^3\underline{k}_i\,d^3\underline{k}_f. \qquad (2.11)$$

However, due to the simplification in expressions achieved by considering our idealized experiment we return to its use, keeping in mind that the final calculations must include these resolution effects.

We now make the main approximation of this approach by writing the transition probability per unit time as that given by the damping theory,[4] which, unlike the conventional perturbation theory, takes explicit account of the decay in time of the quantum states. Hence,

$$W_{n_f n_i}=2\,\frac{|\langle n_f|V^n+H'|n_i\rangle|^2\,\gamma_{n_f n_i}}{(\mathcal{E}^S+\epsilon_n-S_{n_f n_i})^2+\gamma^2_{n_f n_i}}\,, \qquad (2.12)$$

where

$$\begin{aligned}\mathcal{E}^S&=E_i^S-E_f^S,\\ \epsilon_n&=E_i-E_f=\frac{\hbar^2}{2m}(k_i^2-k_f^2),\end{aligned} \qquad (2.13)$$

and where the width $\gamma_{n_f n_i}$, the shift $S_{n_f n_i}$, and the width-and-shift function Γ_{n_i} are

$$\begin{aligned}\gamma_{n_f n_i}&=\left|\mathcal{I}m\left[\lim_{\epsilon\to 0^+}(\Gamma_{n_f}-\Gamma_{n_i})\right]\right|,\\ S_{n_f n_i}&=\mathcal{R}e\left[\lim_{\epsilon\to 0^+}(\Gamma_{n_f}-\Gamma_{n_i})\right],\end{aligned} \qquad (2.14)$$

$$\Gamma_{n_i}=\langle n_i|V^n+H'|n_i\rangle-\sum_{n\neq n_i}\frac{|\langle n|V^n+H'|n_i\rangle|^2}{E_n^S-E_{n_i}^S+i\epsilon}\,.$$

If the intermediate state summation on the label involves a continuous label such as $\underline{k}$, the wave vector of a plane wave, then the summation on that label is to be replaced by an integration and the integral is to be interpreted as illustrated in the following example:

$$\sum_{\eta} \to \sum_{\underline{\mathbf{k}}} \to \left(\frac{L}{2\pi}\right)^3 \int \frac{d^3\mathbf{k}\,|\langle \mathbf{k}|V^n+H'|\mathbf{k}_i\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}_i}+i\epsilon},$$

$$=\sqrt{2}\left(\frac{M}{\hbar^2}\right)^{3/2}\left(\frac{L}{2\pi}\right)^3 \int \frac{dE_{\mathbf{k}}\,E_{\mathbf{k}}^{1/2}\,|\langle \mathbf{k}|V^n+H'|\mathbf{k}_i\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}_i}+i\epsilon},$$

$$=\sqrt{2}\left(\frac{M}{\hbar^2}\right)^{3/2}\left(\frac{L}{2\pi}\right)^3 \left[\mathbb{P}\int \frac{dE_{\mathbf{k}}\,E_{\mathbf{k}}^{1/2}\,|\langle \mathbf{k}|V^n+H'|\mathbf{k}_i\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}_i}} \right. \tag{2.15}$$

$$\left. -i\pi E_{\mathbf{k}_i}^{1/2}\,|\langle \mathbf{k}|V^n+H'|\mathbf{k}_i\rangle|^2_{E_{\mathbf{k}}=E_{\mathbf{k}_i}}\right],$$

where $\mathbb{P}$ is the Cauchy principal value operator.

In contrast to the damping theory result, recall that first order perturbation theory gives

$$W_{\eta_f\eta_i} = \frac{2\pi}{\hbar}|\langle\eta_f|V^n+H'|\eta_i\rangle|^2\,\delta(E_i-E_f+E_i^s-E_f^s).$$

It is easily seen that the energy conserving delta function is replaced in the damping theory by a peaked function.

However, (2.10) may be further reduced. Since H' does not depend on neutron coordinates, and since the initial and final neutron states are not identical, $\langle\eta_f|H'|\eta_i\rangle = 0$. Thus, we now need to specify the neutron-nuclear interaction potential. For sufficiently low energy neutrons ($E_i \lesssim$ ev) whose wavelengths are large compared to the range of nuclear forces and for which nuclear scattering is isotropic in the center-of-mass coordinate system and independent of neutron energy, neutron-nuclear collisions may be considered to be "localized impacts" so that use of the "Fermi pseudopotential"[5] for V^n is appropriate. Then

$$V^n = \frac{2\pi\hbar^2}{m}\sum_{\ell\alpha} a_{\ell\alpha}\,\delta(\underline{r}-\underline{R}_{\ell\alpha}), \tag{2.16}$$

where $a_{\ell\alpha}$ is the scattering length of the α^{th} nucleus in the ℓ^{th} molecule, whose position coordinate is $\underline{R}_{\ell\alpha}$, and summation is over all the nuclei and molecules in the scatterer. In general, the scattering length $a_{\ell\alpha}$ is spin-dependent:

$$a_{\ell\alpha} = A_{\ell\alpha} + B_{\ell\alpha}(\underline{\tau}\cdot\underline{S}_{\ell\alpha}), \tag{2.17}$$

where $\underline{\tau}$ and $\underline{S}_{\ell\alpha}$ are respectively the neutron and nuclear spin, and $A_{\ell\alpha}$ and $B_{\ell\alpha}$ are nuclear constants.

Use of the Fermi pseudopotential has been evaluated as to accuracy by Breit, et al.,[6] by Lippman,[7] and by Plummer and Summerfield,[8] all of whom report it is accurate to .3% for neutron energies up to .4 ev in the first Born approximation development. Thus the simpler zero-range pseudopotential is generally used for slow-neutron scattering rather than a short-range Yukawa potential with which the scattering length becomes energy dependent. The form of the pseudopotential is chosen to guarantee that when used with the first Born approximation the correct total scattering cross section for a free atom is obtained in the high-energy limit ($E_i >$ ev), viz., $\sigma_T = 4\pi a_f^2$, where a_f is the free-atom scattering length which must be determined experimentally. The so-called bound-atom scattering length is $a_b = (m+M/M)a_f$ where M is the mass of the scatterer.

The matrix element of V^n then reduces to

$$\frac{2\pi\hbar^2}{m L^3}\langle f\tau_f|\sum_{\ell\alpha} a_{\ell\alpha}\, e^{i\underline{\kappa}\cdot\underline{R}_{\ell\alpha}}|i\tau_i\rangle,$$

where $\underline{\kappa} = \underline{k}_i - \underline{k}_f$, so that the differential cross section may be written as

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{2\pi N k_i}\sum_{\tau_f,\tau_i}\sum_{i,f} P_i \frac{\left|\langle f\tau_f|\sum_{\ell\alpha} a_{\ell\alpha}\, e^{i\underline{\kappa}\cdot\underline{R}_{\ell\alpha}}|i\tau_i\rangle\right|^2 \gamma_{n_f n_i}}{(\mathcal{E}^s + \epsilon_n - S_{n_f n_i})^2 + \gamma^2_{n_f n_i}} \qquad (2.18)$$

Separation of spin and coordinate dependences is not always allowed. Spin correlation effects may be neglected, however, for all but the lightest diatomic molecules containing like nuclei at very low temperatures,[9] so that the spin and spatial states of the scatterer are here assumed to be separable. Still, the summation over the final spin states cannot be performed because the width $\gamma_{n_f n_i}$ and shift $S_{n_f n_i}$ are spin-dependent as well as $a_{\ell\alpha}$. However, when the width and shift due to the neutron-nucleus interaction are neglected, the summation over all the spin states becomes simply

$$\frac{1}{2}\sum_{s_i,\tau_i} P_{s_i}\langle s_i\tau_i|a_{\ell\alpha}a^{+}_{\ell'\alpha'}|s_i\tau_i\rangle,$$

where $|s_i\rangle$ denotes the initial spin state of the scatterer, and hence the spin dependence of the neutron-nucleus interaction does not influence the line shape. By noting that

$$\sum_{\tau_i} \langle \tau_i | \underline{\tau} \cdot \underline{S}_{\ell\alpha} | \tau_i \rangle = 0,$$

$$\frac{1}{2} \sum_{\tau_i} \langle \tau_i | (\underline{\tau} \cdot \underline{S}_{\ell\alpha})(\underline{\tau} \cdot \underline{S}_{\ell'\alpha'}) | \tau_i \rangle = \frac{1}{4} S_{\ell\alpha}(S_{\ell\alpha}+1)\delta_{\ell\ell'}\delta_{\alpha\alpha'}, \tag{2.19}$$

the spin state summation becomes

$$\frac{1}{2} \sum_{\tau_i} \langle \tau_i | a_{\ell\alpha} a^{+}_{\ell'\alpha'} | \tau_i \rangle = A_{\ell\alpha} A_{\ell'\alpha'} + \frac{1}{4} B^{2}_{\ell\alpha} S_{\ell\alpha}(S_{\ell\alpha}+1)\delta_{\ell\ell'}\delta_{\alpha\alpha'} \tag{2.20}$$

where, when substituted into the above average over the $|s_i\rangle$ states, yields the quantities $A_{\ell\alpha}$ and $B_{\ell\alpha}\sqrt{S_{\ell\alpha}(S_{\ell\alpha}+1)}/2$, and leads to a convenient separation of the cross section of (2.18) into various contributions as follows:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{\pi N k_i} \Big\{ \sum_{\ell\alpha} D^{2}_{\ell\alpha} \sum_{i,f} P_i I_{\ell\alpha} I^{*}_{\ell\alpha} \Xi_{fi}$$

$$+ \sum_{\ell} {\sum_{\alpha\alpha'}}' A_{\ell\alpha} A_{\ell\alpha'} \sum_{i,f} P_i I_{\ell\alpha} I^{*}_{\ell\alpha'} \Xi + {\sum_{\ell\ell'}}' \sum_{\alpha\alpha'} A_{\ell\alpha} A_{\ell'\alpha'} \sum_{i,f} P_i I_{\ell\alpha} I^{*}_{\ell'\alpha'} \Xi_{fi} \Big\}, \tag{2.21}$$

where the prime over the summation indicates that terms for which the two indices become equal are to be omitted, and where

$$I_{\ell\alpha} = \langle f | e^{i\underline{\kappa} \cdot \underline{R}_{\ell\alpha}} | i \rangle,$$

$$\Xi_{fi} = \frac{\gamma_{fi}}{(\mathcal{E}^{s} + \epsilon_n - S_{fi})^2 + \gamma_{fi}^{2}}, \tag{2.22}$$

$$D^{2}_{\ell\alpha} = A^{2}_{\ell\alpha} + \frac{1}{4} B^{2}_{\ell\alpha} S_{\ell\alpha}(S_{\ell\alpha}+1).$$

The three terms in (2.21) correspond to direct scattering, "inner" scattering, which is interference scattering within the same molecule, and "outer" scattering which is interference from different molecules. The nuclear constants $A_{\ell\alpha}$ and $B_{\ell\alpha}\sqrt{S_{\ell\alpha}(S_{\ell\alpha}+1)}/2$ are respectively called the coherent and incoherent scattering amplitudes. Separation into contributions from coherent and incoherent scattering can now be accomplished with a rearrangement of (2.21) as direct scattering is both coherent and incoherent due to spin effects while interference scattering is only coherent. Exhibiting the coherent and incoherent contributions as separate terms (2.21) becomes

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{\pi N k_i}\Big\{\sum_{\ell\ell'}\sum_{\alpha\alpha'} A_{\ell\alpha}A_{\ell'\alpha'}\sum_{i,f} P_i I_{\ell\alpha} I^*_{\ell'\alpha'}\,\Xi_{fi} \qquad (2.23)$$

$$+\sum_{\ell\alpha}\frac{1}{4}B^2_{\ell\alpha}S_{\ell\alpha}(S_{\ell\alpha}+1)\sum_{i,f} P_i I_{\ell\alpha} I^*_{\ell\alpha}\,\Xi_{fi}\Big\}.$$

When the scatterer contains more than one isotope appropriate isotopic averages of the scattering amplitudes should be used.[10]

Thus, (2.21) is the general result desired and provides a basis for direct calculations of the quantity measured in a scattering experiment. It is basically the equation obtained by Akcasu. It offers an approximate description which is sufficiently accurate to include the broadening and the shift of the lines which may be present in the energy distribution of the inelastically scattered neutrons. Whether such spectral lines exist or not depends on the nature of the scatterer, since only transitions between discrete states give rise to lines or peaks in the energy distribution.* These lines may not be recognizable in the actual measured distribution due to the broadening and overlapping of adjacent lines caused either by the intermolecular interactions or by the finite resolution of the experimental apparatus, but in any case (2.21) furnishes a valid and powerful tool in the analysis of neutron scattering. It will be seen that (2.21) provides a computational framework which is more interpretable physically than other approaches.

2.3 THE CONVENTIONAL FORMULATIONS

In this regard, we briefly review the two conventional general formulations of neutron scattering as developed by Zemach and Glauber,[11] and Van Hove,[12] and display the connection between them. Both formulations make the same assumptions made in the line shape formulation concerning the effects of multiple scattering and the statistics obeyed by the scatterer, which have recently been investigated by Plummer.[13] Also, both formulations are based on the Fermi approximation, i.e., the use of the Fermi pseudopotential to represent the neutron-nucleus interaction in the first Born approximation description of the scattering.

Zemach and Glauber, in treating those systems which can be characterized by the degrees of freedom appropriate to gas molecules, employ the formalism of the first Born approximation to write the cross section

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*Yip and Nelkin[14] have recently commented on the implications for liquids of a sound-wave peak in the energy distribution for a gas.

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i N} \sum_{i,f} P_i \left| f_{fi} \right|^2 \delta(\epsilon_n - \mathcal{E}^s), \tag{2.24}$$

where the amplitude of the scattered neutron wave is

$$f_{fi} = -\frac{m}{2\pi\hbar^2} \int d^3r' \, e^{i\underline{\kappa}\cdot\underline{r}'} \langle f | V^n | i \rangle, \tag{2.25}$$

and where

$$V^n = \frac{2\pi\hbar^2}{m} \sum_{\ell\alpha} a_{\ell\alpha} \, \delta(\underline{r}' - \underline{R}_{\ell\alpha}),$$

are the Fermi pseudopotentials. Using the Fourier representation of the delta function

$$\delta(x) = \frac{1}{2\pi\hbar} \int dt \, e^{-\frac{itx}{\hbar}},$$

and doing the sum over final states of the system using their completeness property, the general result is

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{2\pi\hbar} \frac{k_f}{k_i} \int dt \, e^{-i\epsilon_n \frac{t}{\hbar}} \frac{1}{N} \sum_{\ell\ell'} \langle \chi_{\ell\ell'} \rangle_T, \tag{2.26}$$

where the intermediate scattering function,

$$\langle \chi_{\ell\ell'} \rangle_T = \sum_i P_i \langle i | \sum_{\alpha\alpha'} a_{\ell\alpha} a_{\ell'\alpha'} e^{i\underline{\kappa}\cdot\underline{R}_{\ell'\alpha'}(t)} e^{-i\underline{\kappa}\cdot\underline{R}_{\ell\alpha}} | i \rangle, \tag{2.27}$$

is written to emphasize that the observable neutron interaction is with a molecule, not the individual nuclei of the molecule separately, and that the operator whose matrix elements appear in the initial state average involves the sum of the ordered pairs of nuclei α and α'. This initial state average is usually referred to as a thermal average because the scattering sample is assumed to be in thermodynamic equilibrium. The Heisenberg operator $\underline{R}_{\ell'\alpha'}(t)$ is defined by

$$\underline{R}_{\ell'\alpha'}(t) = e^{i\frac{t}{\hbar}\mathcal{H}^s}\,\underline{R}_{\ell'\alpha'}\,e^{-i\frac{t}{\hbar}\mathcal{H}^s}, \qquad (2.28)$$

and the matrix elements appearing in the thermal average are expressed in the representation generated by $\mathcal{H}^s$, which depending on the approach used may include none, some, or all of H'. The rest of H', if any, is ignored in this formulation.

In order to generalize the Zernike-Prins[15] "static approximation" formula to scattering processes in which energy transfers are not negligible in comparison with the energy of the incident neutron, Van Hove introduced space-time pair distribution functions defined for a monatomic system* by

$$G(\underline{r},t) = \frac{1}{N}\left\langle \sum_{\ell=1}^{N} \int d^3r'\,\delta(\underline{r}+\underline{R}_\ell-\underline{r}')\,\delta(\underline{r}'-\underline{R}_\ell(t))\right\rangle_T, \qquad (2.29)$$

where the Heisenberg operators and thermal average are given as in (2.28) and (2.27) except the operators are different in (2.27). The cross section can then be written in terms of $G(\underline{r},t)$ by means of the so-called "scattering law," $S(\underline{\kappa},\omega)$, which is the four-dimensional Fourier transform of $G(\underline{r},t)$:

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*Vineyard[18] has discussed the generalization to polyatomic systems.

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{a^2 k_f}{\hbar k_i} S(\underline{\kappa},\omega),$$

$$S(\underline{\kappa},\omega) = \frac{N}{2\pi}\int dt\, d^3r\, G(\underline{r},t)\, e^{i(\underline{\kappa}\cdot\underline{r}-\omega t)}, \qquad (2.30)$$

where the symbol a is used to denote the appropriate bound atom scattering length. An advantage of this formulation is that $G(\underline{r},t)$ may be interpreted physically in the classical limit and certain methods of calculation not otherwise accessible are obtained. Rosenbaum and Zweifel[16,17] have commented on and reviewed the various prescriptions which have been proposed to establish a relationship between the classical $G_c(\underline{r},t)$ and the cross section. They find that the dominant correction to the cross section, when $G(\underline{r},t)$ is replaced by $G_c(\underline{r},t)$ as given in the Vineyard prescription,[18] is given by the factor $e^{\epsilon_n/2k_BT}e^{-(\Delta p)^2/8Mk_BT}$, which is significant for large energy transfer ϵ_n, large momentum transfer Δp, and scatterers of small mass M.

Briefly, we mention that the scattering law is conventionally written[19,20] as a function of only two dimensionless variables α and β where

$$\alpha = \frac{m}{Mk_BT}\left[E_i + E_f - 2\cos\theta\sqrt{E_iE_f}\right]; \quad \beta = \frac{E_i - E_f}{k_BT}. \qquad (2.31)$$

That is, for one nuclear species as scatterer

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\sigma_b}{4\pi}\sqrt{\frac{E_f}{E_i}}\, e^{-\beta/2} S(\alpha,\beta), \qquad (2.32)$$

where $S(\alpha,\beta)$ is given as the Fourier transform of a characteristic function,

$$e^{-\beta/2} S(\alpha,\beta) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} I(\alpha,t)\, e^{-i\beta t}\, dt, \tag{2.33}$$

where in the incoherent approximation

$$I(\alpha,t) = e^{-\alpha W(t)}, \tag{2.34}$$

with the width function $W(t)$ given in turn by

$$W(t) = \int_0^\infty \rho(\epsilon)\, \frac{\cosh\left(\frac{\epsilon}{2k_BT}\right) - \cos\left(\frac{\epsilon}{k_BT}\right)}{\frac{\epsilon}{k_BT}\sinh\left(\frac{\epsilon}{2k_BT}\right)}\, d\epsilon, \tag{2.35}$$

where $\rho(\epsilon)$ is an energy-distribution function. Two recent papers[21,22] have commented on various numerical methods employed in connection with (2.32).

The essential connection between the Zemach and Glauber formalism and that used by Van Hove can now be indicated by noting that from (2.26) the cross section for a monatomic system is

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \frac{a^2 k_f}{2\pi N k_i}\int \frac{dt}{\hbar}\, e^{-i\epsilon_n \frac{t}{\hbar}} \sum_{\ell\ell'} \left\langle e^{i\underline{\kappa}\cdot\underline{R}_{\ell'}(t)}\, e^{-i\underline{\kappa}\cdot\underline{R}_{\ell}} \right\rangle_T, \tag{2.36}$$

and by comparing (2.30) with (2.36)

$$G(\underline{r},t) = \frac{1}{(2\pi)^3 N}\int d^3\kappa\, e^{-i\underline{\kappa}\cdot\underline{r}} \sum_{\ell\ell'} \left\langle e^{i\underline{\kappa}\cdot\underline{R}_{\ell'}(t)}\, e^{-i\underline{\kappa}\cdot\underline{R}_{\ell}} \right\rangle_T. \tag{2.37}$$

2.4 THIS APPROACH

We now proceed to consider (2.21) again but this time giving specific attention to the final state summation and the initial state average which appears in each term. We have explicitly

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \frac{k_f}{\pi N k_i} \sum_{ll'\alpha\alpha'} C_{ll'\alpha\alpha'}\, T_{ll'\alpha\alpha'}, \tag{2.38}$$

where

$$T_{ll\alpha\alpha} = \sum_{i,f} P_i \frac{|\langle f|\, e^{i\underline{K}\cdot\underline{R}_{l\alpha}}\, |i\rangle|^2\, \gamma_{fi}}{(E_i^S - E_f^S + \epsilon_n - S_f + S_i)^2 + \gamma_{fi}^2},$$

$$= \sum_{i,f} P_i |\langle f|\, e^{i\underline{K}\cdot\underline{R}_{l\alpha}} |i\rangle|^2 \int_{-\infty}^{+\infty} \frac{\delta(\rho - \{E_f^S - E_i^S + S_f - S_i\}/\hbar)\, \gamma_{fi}}{(\epsilon_n - \hbar\rho)^2 + \gamma_{fi}^2}\, d\rho, \tag{2.39}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \sum_{i,f} P_i\, |\langle f|\, e^{i\underline{K}\cdot\underline{R}_{l\alpha}}\, |i\rangle|^2 e^{-i\frac{t}{\hbar}\{E_i^S - E_f^S + S_i - S_f\}}$$

$$(\times) \int_{-\infty}^{+\infty} \frac{e^{-it\rho}\, \gamma_{fi}}{(\epsilon_n - \hbar\rho)^2 + \gamma_{fi}^2}\, d\rho .$$

The integral over ρ can be written

$$I_\gamma = \int_{-\infty}^{+\infty} \frac{e^{-it\rho}}{(\epsilon_n - \hbar\rho + i\gamma_{fi})(\epsilon_n - \hbar\rho - i\gamma_{fi})}\, d\rho, \tag{2.40}$$

where the singularities of the integrand are $\rho = (\epsilon_n + i\gamma_{fi})/\hbar$, $(\epsilon_n - i\gamma_{fi})/\hbar$.

The integral I_γ can be evaluated using the contours shown in Fig. 1, where the upper contour is used for $t < 0$ and the lower for $t > 0$.

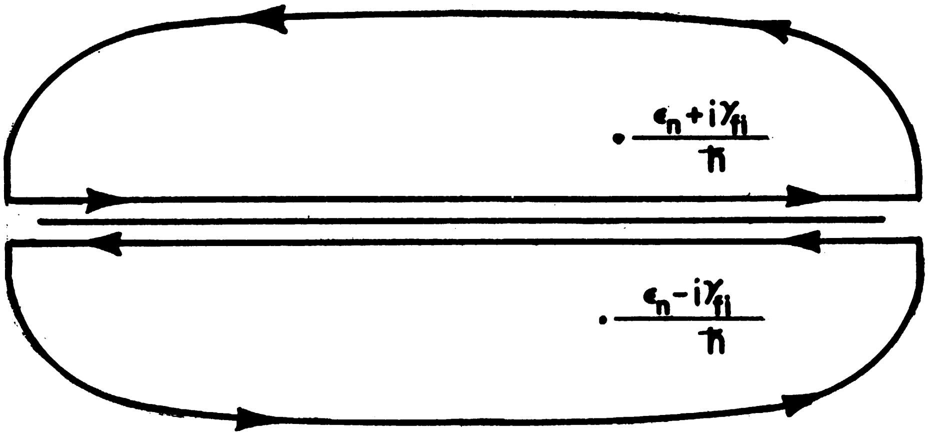


Fig. 1. Contours for evaluation of I_γ.

From the calculus of residues, Cauchy's integral formula allows us to write

$$T_{\ell\ell'\alpha\alpha'} = \frac{1}{2}\sum_{i,f} P_i \int_{-\infty}^{+\infty} e^{-i\frac{t}{\hbar}\epsilon_n - \gamma_{fi}\frac{|t|}{\hbar}} \langle i| e^{i\frac{t}{\hbar}\mathcal{H}^s} e^{i\frac{t}{\hbar}\mathcal{S}} e^{-i\underline{\kappa}\cdot\underline{R}_{\ell'\alpha'}} e^{-i\frac{t}{\hbar}\mathcal{S}} e^{-i\frac{t}{\hbar}\mathcal{H}^s} |f\rangle \tag{2.41}$$

$$(x) \langle f| e^{i\underline{\kappa}\cdot\underline{R}_{\ell\alpha}} |i\rangle dt,$$

where we have further used the relations

$$e^{i\frac{t}{\hbar}E_f^s} |f\rangle = e^{i\frac{t}{\hbar}\mathcal{H}^s} |f\rangle,$$
$$e^{i\frac{t}{\hbar}S_f} |f\rangle = e^{i\frac{t}{\hbar}\mathcal{S}} |f\rangle, \tag{2.42}$$

and the latter relations formally define the operator $\mathcal{S}$, which is diagonal in the representation generated by $\mathcal{H}^s$.

We note that the operators in (2.41) correspond to a time-independent operator $e^{i\underline{\kappa}\cdot\underline{R}}$ and its corresponding time-dependent Heisenberg operator, defined as

$$e^{-i\underline{\kappa}\cdot\underline{R}'(t)} = e^{i\frac{t}{\hbar}H''}\, e^{-i\underline{\kappa}\cdot\underline{R}}\, e^{-i\frac{t}{\hbar}H''}, \tag{2.43}$$

where $\underline{R}'(t)$ is a solution of

$$i\hbar\,\frac{d\underline{R}'(t)}{dt} = \left[\underline{R}'(t), H''\right], \tag{2.44}$$

and where $H'' = \mathcal{H}^{s} + \mathcal{S}$, is not the complete Hamiltonian H^{s} of the system only because of the fact that in using the damping theory for prescribing a method for estimating S_i and S_f, we have essentially replaced part of the effect of H' by $\mathcal{S}$ which depends in a complicated way on H' and which commutes with $\mathcal{H}^{s}$. Part of the effect of H' has also been used in defining the width γ_{fi}.

At this point we can exhibit explicitly that in the limit of zero width and shift ($\gamma_{fi} = 0$, $\mathcal{S} = 0$ which imply that $H' = 0$ and hence $\mathcal{H}^{s} \equiv H^{s}$), Equations (2.41) and (2.38) yield precisely (2.26) and (2.27) which is the Zemach and Glauber result.

However, in order to carry the line shape analysis further without specific forms for H', approximation of (2.41) appears unavoidable at this stage. Of course, models might be introduced here in attempts to formulate H' for a given problem. Akcasu and Osborn[23] have done this for crystals by taking into account anharmonic forces. For liquids the appropriate model is less evident. Approximations of (2.41) will, in general, be dictated by the specific application, and hence we leave this further work for Chapter V in which we discuss the line shape problem for hindered rotational transitions of diatomic molecules in liquids after giving our attention to the detailed description of rotations.

But, first we will now specifically make the assumption that the energy of the system can be represented as the sum of individual molecular energies which themselves can be separated into energies of translation, rotation, and vibration. Vibration-rotation interactions are thus neglected. Thus, we write

$$\mathcal{H}^S = \sum_{\ell} \mathcal{H}_{\ell}^S, \tag{2.45}$$

with

$$\mathcal{H}_{\ell}^S = \mathcal{H}_T^{\ell} + \mathcal{H}_R^{\ell} + \mathcal{H}_V^{\ell}. \tag{2.46}$$

Thus the physical many-body problem is reduced to a problem in which both the dominant features and the perturbation have an equivalent single-particle-plus-potentials description allowing inclusion of many-body effects.

The form of the molecular Hamiltonian (2.46) suggests that the position of a nucleus measured in the laboratory coordinate system may be written

$$\underline{R}_{\ell\alpha} = \underline{R}_{\ell} + \underline{b}_{\ell\alpha} + \underline{u}_{\ell\alpha}, \tag{2.47}$$

where $\underline{R}_{\ell}$ is the position of the center-of-mass of the ℓ^{th} molecule, $\underline{b}_{\ell\alpha}$ is the equilibrium position of the α^{th} nucleus in the ℓ^{th} molecule, and

$\underline{u}_{\ell\alpha}$ is its instantaneous displacement from equilibrium. When the molecule consists of three atoms or more, nuclear vibrations can be treated in terms of normal coordinates,[24] which are obtained by a transformation of the form:

$$\underline{u}_{\ell\alpha} = \sum_{\lambda} \underline{C}^{\lambda}_{\ell\alpha} q_{\lambda} \tag{2.48}$$

where $\underline{C}^{\lambda}$ is the λ^{th} polarization vector associated with normal coordinate q_{λ}. We note that $\underline{R}_{\ell}$, $\underline{b}_{\ell\alpha}$, q_{λ} will not commute with $\mathcal{H}^{\ell}_{T}$, $\mathcal{H}^{\ell}_{R}$, $\mathcal{H}^{\ell}_{V}$, respectively, and $\underline{C}_{\ell\alpha}$, a vector which rotates with the molecule, also will not commute with $\mathcal{H}^{\ell}_{R}$. All other commutators not involving H' are zero.

In what follows, we will focus on the rotational degrees of freedom of molecules and explore specific dynamical models describing the dominant aspects of molecular rotations and the refinements in these models and descriptions needed to give rise to line shape.

CHAPTER III

SLOW-NEUTRON SCATTERING AND INTERNAL ROTATION IN GASES AND NORMAL LIQUIDS

> "The study of a physical system essentially consists in solving its time-independent Schroedinger equation."
>
> ---A. Messiah (1961)

3.1 INTRODUCTION

The energy distribution of scattered neutrons can be significantly influenced by angular momentum exchanges which result from neutron interaction with the rotational degrees of freedom of the scattering molecule. We adopt the semi-rigid model of a molecule in which, for purposes of discussing rotations, the molecule is taken to consist of one or more rigid parts, while in discussing vibrations the molecule is taken to consist of atoms oscillating about equilibrium positions. In order to achieve an understanding of the rotational dynamics which will then allow an application of the refinements present in the line shape formalism, we adopt in this and the following chapter the limit of zero line width and shift which is identical with the formalism of Zemach and Glauber.

The problem of inelastic neutron scattering by rigid molecules rotating freely in space has been treated by many authors using various formulations. Sachs and Teller[25] developed a theory of neutron scattering by molecules considered as rigid classical free rotators. The Zemach and Glauber formalism was used by Krieger and Nelkin,[26] whose theory of neutron scattering by molecules treated molecular vibrations quantum mechanically, but translation and free rotation classically. Theories of neutron scattering by molecules which take into consideration the quantum nature of the rigid molecule rotational degrees of freedom have been developed by Volkin,[27] Rahman,[28] and Griffing.[29] Further, theories of neutron scattering by some special molecules have been given by Brimberg,[30] Lovseth,[31] and Messiah.[32]

We shall begin with a review of the dynamics of free molecular rotations ignoring for the present the translational and vibrational degrees of freedom. The purpose for the review is twofold. First, those aspects of the molecular rotation problem relevant to the analysis of neutron scattering can be presented. Second, some of the discussion of descriptions of hindered motions given later depends on certain features of the free rotation development. Following this review, we will discuss the problem of internal rotation and its study by neutron scattering.

The study of internal rotation of one part of a molecule with respect to the rest of the molecule has been a subject of interest for more than thirty years and numerous methods have been devised for investigating this phenomenon. Internal rotation interacts with the over-all rotation of a molecule and produces certain effects which may be observed by inelastic neutron scattering. Potential barriers hindering internal rotation are presumably caused by the interactions of two groups of electrons and nuclei. In principle, the barrier heights can be obtained by straightforward quantum-mechanical calculations, but the mathematical complexity is so great that a rigorous computation is impractical at present. The alternative approach is to try to describe the origin of the barriers in terms of the forces which appear in the study of intermolecular interactions. Many such analyses have been published,[33,34] but the results are not completely satisfying. Moreover, the study of molecules possessing internal rotational degrees of freedom in the liquid state is, in general, further complicated by true intermolecular interactions.

Recent interest in the behavior of hydrogenous liquids as thermal neutron nuclear reactor moderators has led to investigations of the neutron-scattering characteristics of organic molecules including the lower alcohols, methanol, ethylanol, etc.,[35,36,37] which show broad inelastic bands tentatively called "rotation" bands. These molecules possess an internal rotational degree of freedom. In some cases infrared and Raman spectra[38] have been used to determine the frequencies of the internal torsional oscillations. In principle, this would be the direct method for rotational dynamics studies to determine the torsional frequencies and the potential barriers. Unfortunately, these torsional oscillations are usually inactive and lie in the very far infrared region (low energy) so that their detection and assignment are usually difficult, if at all possible. Nuclear magnetic resonance[39-42] also has been used recently to give a measure of the magnitude of barriers in liquids. Barrier heights in the range of .15 to .75 ev may be determined by measuring the widths of the resonance lines as functions of temperature. The time scale of NMR is such that if the barrier height is less than about .15 ev, the internal rotation appears to be free.

Such thermodynamic properties as entropy and vapor heat capacity are probably the most commonly used to calculate barrier heights[43,44] and are applicable for molecules with high barriers (greater than ~.1 ev). The most accurate of the common methods of determining barrier heights which has been increasingly employed in the last ten years is microwave spectroscopy,[45] but its use is limited primarily to the gaseous state and then only to polar molecules. Quite recently J. J. Rush and co-workers[46-54] have studied the internal barriers in solids and liquids by the neutron total cross section technique at very long wavelengths. In an experimental study of rotations of certain molecular groups in condensed systems, Janik, et al.,[55] in order to interpret their results were forced to assume some substances could be used as standards of rotational freedom or hindrance in comparison with others treated as rotational "unknowns." Such measures will not be necessary with a theory such as is presented here.

The interest in the description of slow-neutron inelastic scattering from such molecules is hence a twofold one. First, the description of the differential scattering cross section is important from the standpoint of predictions which allow reactor physicists to make more detailed and accurate calculations. Second, the neutron scattering method may extend present capabilities in studying internal rotational dynamics of molecules and thereby intermolecular forces, but only if an accurate description can be achieved.

In the internal rotation of molecules such as ethane, CH_3-CH_3, one methyl group can rotate into one of the three positions which are equivalent with respect to the other methyl group. If each of these configurations were considered independent, the torsional energy levels would all be triply degenerate. However, the quantum-mechanical tunneling effect splits each torsional level in asymmetric molecules into nondegenerate and degenerate sublevels. Associated with each of the torsional sublevels, one has a set of energy levels arising from the over-all rotation of the entire molecule, these levels being referred to as over-all rotational levels. To facilitate understanding we will differentiate between three classes of internal rotation. Torsion is any kind of internal rotation. Torsional oscillation implies a state in the lower part of a high barrier, free internal rotation implies a state well above any barrier, and hindered internal rotation implies the intermediate cases. Usage also defines, in addition to the above specific meaning, that hindered internal rotation applies to the general case of the existence of an internal barrier regardless of the state of occupation.

3.2 FREE ROTATIONS OF RIGID MOLECULES

Rotating bodies are classified according to relations between their principal moments of inertia I_x, I_y, I_z where these are defined with respect to that system of axes fixed in the body which coincide with the principle axes. For linear molecules

$$I_x = I_y, \quad I_z = 0,$$

while for symmetric molecules

$$I_x = I_y \neq I_z, \quad I_z \neq 0,$$

and for asymmetric molecules

$$I_x \neq I_z, I_x \neq I_y \neq I_z, \{I_x, I_y, I_z\} \neq 0,$$

and finally for spherical molecules

$$I_x = I_y = I_z, \quad I_z \neq 0.$$

Now consider a rigid polyatomic molecule rotating freely in space. Its Hamiltonian is

$$H_{FR} = \frac{L_x'^2}{2I_x} + \frac{L_y'^2}{2I_y} + \frac{L_z'^2}{2I_z}, \tag{3.1}$$

where the L's are the body system components of the total angular momentum. It is conventional to write[56,57]

$$\frac{2}{c} H_{FR} = aL'^2 + L_z'^2 + b(L_x'^2 - L_y'^2), \tag{3.2}$$

where

$$a=\frac{1}{2c}\left(\frac{1}{I_x}+\frac{1}{I_y}\right),$$

$$b=\frac{1}{2c}\left(\frac{1}{I_x}-\frac{1}{I_y}\right),$$

$$c=\frac{1}{I_z}-\frac{1}{2}\left(\frac{1}{I_x}+\frac{1}{I_y}\right)$$

The symmetric molecule $(I=I_x=I_y)$ and spherical molecule $(I=I_x=I_y=I_z)$ Hamiltonians are also contained in (3.2). The Euler angles[58] $(\phi\theta\varphi)$ which specify the orientation of the body axes relative to a space coordinate system (see Fig. 2.) are dynamical variables in terms of which the angular momentum operators can be expressed (see Appendix F).

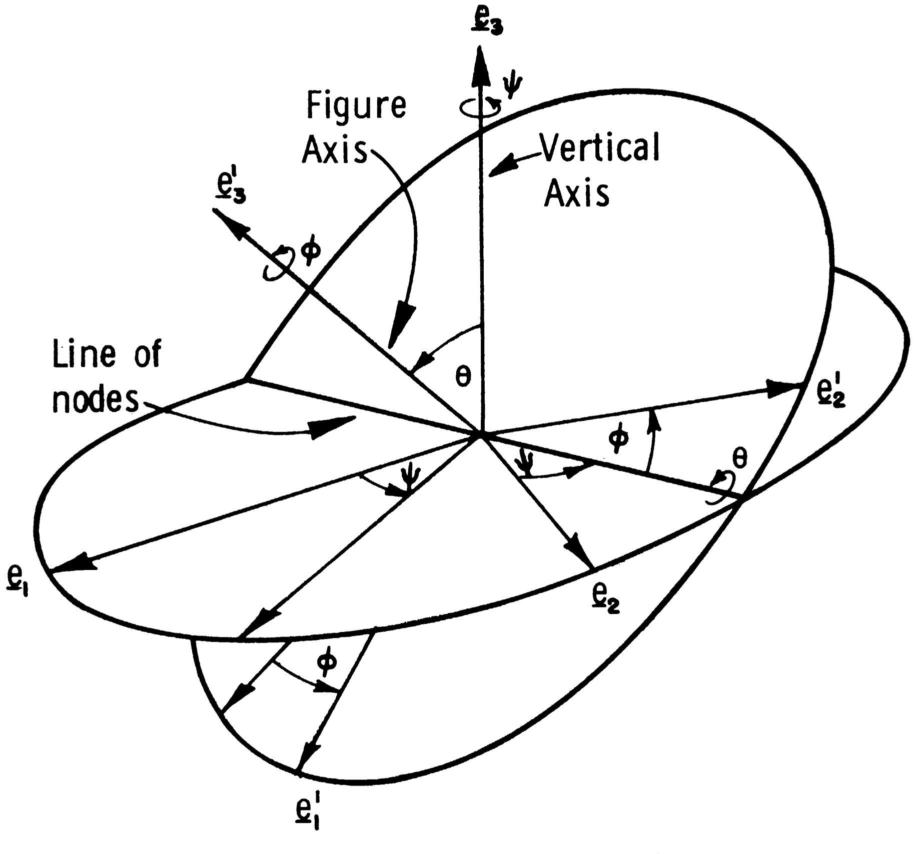


Fig. 2. Euler angles $(\phi\ \theta\ \varphi)$.

The eigenvalue problem for a rigid symmetric molecule is

$$\left(H_{FSR} - E\right)\Phi(\psi\theta\varphi) = 0, \tag{3.3}$$

where from (3.2) with $I=I_x=I_y$

$$H_{FSR} = \frac{L'^2}{2I} + \frac{(I-I_z)}{2II_z} L_z'^2, \tag{3.4}$$

in terms of Euler angles

$$H_{FSR} = -B\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right) + \frac{I-I_z}{I_z}\frac{\partial^2}{\partial\varphi^2}\right], \tag{3.5}$$

where $B = h^2/2I$. Equation (3.3) is separable due to the form of (3.5). Therefore,

$$\Phi(\psi\theta\varphi) = \Phi_1(\psi)\Phi_2(\varphi)\Theta(\theta) \tag{3.6}$$

and in a straightforward manner

$$\Phi_1(\psi) = e^{iM\psi}, \tag{3.7}$$

$$\Phi_2(\varphi) = e^{iK\varphi}, \tag{3.8}$$

where due to the commonly employed boundary condition of single-valuedness of the wave function M and K are integers and the equation for $\Theta(\theta)$ is

$$\frac{d^2\Theta}{d\theta^2} + \cot\theta\frac{d\Theta}{d\theta} - \left[\frac{(M-K\cos\theta)^2}{\sin^2\theta} - \eta\right]\Theta = 0, \tag{3.9}$$

where

$$\eta = \frac{E}{B} - \frac{I}{I_z}K^2, \tag{3.10}$$

and M and K are integer quantum numbers corresponding to components of the total angular momentum along the space-z axis and the body-z axis, respectively. The variable transformation $2t = 1 - \cos\theta$ in (3.9) leads to the form

$$t(1-t)\frac{d^2\Phi(t)}{dt^2} + (1-2t)\frac{d\Phi}{dt} - \left[\frac{(M-K+2Kt)^2}{4t(1-t)} - \eta\right]\Phi = 0, \tag{3.11}$$

where $\Theta(\theta) = \Phi(t)$ and the equation has regular singular points at $t = 0$ and $t = 1$ (another regular singular point at infinity is nonphysical since t is defined on the interval 0 to 1). Since the well behaved solutions near the singular points are

$$\Phi(t) \underset{t\to 0}{\widetilde{\quad}} t^{|M-K|/2},$$

$$\underset{t\to 1}{\widetilde{\quad}} (1-t)^{|M+K|/2},$$

the following transformation is suggested

$$\Phi(t) = t^{|M-K|/2}(1-t)^{|M+K|/2}H(t). \tag{3.12}$$

Using (3.12) in (3.11) results in the hypergeometric equation

$$t(1-t)\frac{d^2H(t)}{dt^2} + [\gamma - (\alpha+\beta+1)t]\frac{dH}{dt} - \alpha\beta H(t) = 0, \tag{3.13}$$

where

$$\begin{aligned} \gamma &= |M-K| + 1, \\ \alpha+\beta &= |M-K| + |M+K| + 1, \\ \alpha\beta &= \tfrac{1}{4}(|M+K|+|M-K|)(|M+K|+|M-K|+2) - K^2 - \eta, \end{aligned} \tag{3.14}$$

and $\alpha < \beta$. The analytic solution to (3.13) about $t = 0$ is called the hypergeometric function. Its power series expansion is convergent for $|t| < 1$, and is called the hypergeometric series

$$\begin{aligned} H(t) = 1 &+ \frac{\alpha\beta}{\gamma} t + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)2!} t^2 + \cdots \\ &+ \frac{\alpha(\alpha+1)\cdots(\alpha+p-1)\beta(\beta+1)\cdots(\beta+p-1)}{\gamma(\gamma+1)\cdots(\gamma+p-1)\,p!} t^p + \cdots . \end{aligned} \tag{3.15}$$

For reasons which will become apparent we are not interested in the solution about $t = 1$, but since the wave function must be finite everywhere the hypergeometric series in (15) must terminate thereby giving us Jaccbi polynomials.[59-61] This will be the case if $\alpha = \frac{1}{2}\left\{(|M-K|+|M+K|+1) - \sqrt{1+4K^2+4\eta}\right\}$ is a negative integer or zero. From this condition it follows that the energy eigenvalues are given by

$$E_{JKM} = BJ(J+1) + \frac{B(I-I_z)}{I_z} K^2, \quad (J = 0, 1, \ldots) \tag{3.16}$$

where $J = -\alpha + \frac{1}{2}(|M+K| + |M-K|)$ is the quantum number appropriate to the total angular momentum and the range of K and M is 0, ±1, . . . ,±J. The fact that the energy is independent of M could have been anticipated because the molecule has no preferred orientations is space. The energy is also independent of the sign of K, because the molecule may rotate clockwise or counter-clockwise around its threefold symmetry axis. The orientational degeneracy is 2J+1, hence each state $|JKM>$ is 2(2J+1)-fold degenerate, except the K = 0 states which are only (2J+1)-fold degenerate. The eigenfunctions are

$$|JKM\rangle = N_{JKM} e^{iM\psi} e^{iK\varphi} t^{\frac{|M-K|}{2}} (1-t)^{\frac{|M+K|}{2}} G_{J-\frac{1}{2}(|M+K|+|M-K|)}(t) \tag{3.17}$$

where

$$N^2_{JKM} = \frac{(|M+K|+|M-K|-2\alpha+1)!(|M+K|+|M-K|-\alpha)!(|M-K| \alpha)!}{4\pi^2(-\alpha)!(|M-K|)!(|M+K|-\alpha)}, \tag{3.18}$$

and the Jacobi polynomials, defined on the interval 0 to 1, are polynomials of degree J - $\frac{1}{2}$ (|M+K| + |M-K|), which is integer:

$$G_p(t) = \frac{}{t^{\frac{|M-K|}{2}}(1-t)^{\frac{|M+K|}{2}}\left(\frac{|M-K|}{2}+p\right)!} \frac{d^p}{dt^p}\left[t^{\frac{|M-K|}{2}+p}(1-t)^{\frac{|M+K|}{2}+p}\right]. \tag{3.19}$$

However, Wigner[62] has given a more convenient representation of the normalized symmetric molecule wave functions which in the notation used by Rose[63] is

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^J_{-M,-K}(\psi\theta\varphi), \tag{3.20}$$

where the factored dependence on the Euler angles is given by

$$D^J_{MK} = e^{-iM\psi} d^J_{MK}(\theta) e^{-iK\varphi}, \tag{3.21}$$

and

$$d^J_{MK}(\theta) = \left[(J+K)!(J-K)!(J+M)!(J-M)!\right]^{1/2} \qquad (3.22)$$
$$(\times)\sum_p \frac{(-1)^p\left(\cos\frac{\theta}{2}\right)^{2J+K-M-2p}\left(-\sin\frac{\theta}{2}\right)^{M-K+2p}}{(J-M-p)!(J+K-p)!(p+M-K)!\,p!}$$

where the sum is over the integer p for which the factorial arguments are never negative. The functions D^J_{MK} are called the rotation matrices, and are very useful in the calculation of matrix elements because of their symmetry and transformation properties.[63]

Recalling equations (2.46) and (2.47) and assuming the factoring of the molecular thermal average into thermal averages of translation, rotation, and vibration, the appropriate matrix elements for inner scattering from the ℓth symmetric top molecule are

$$I_{\alpha'}I^*_{\alpha} = \langle JKM|e^{i\underline{\kappa}\cdot\underline{b}_{\alpha'}}|J'K'M'\rangle\langle J'K'M'|e^{-i\underline{\kappa}\cdot\underline{b}_{\alpha}}|JKM\rangle. \qquad (3.23)$$

In the expansion,

$$e^{i\underline{\kappa}\cdot\underline{b}} = 4\pi\sum_{\ell k} i^{\ell} j_{\ell}(\kappa b)\,Y^{k*}_{\ell}(\hat{\underline{b}}')\,Y^{k}_{\ell}(\hat{\underline{\kappa}}'), \qquad (3.24)$$

the prime indicates that the arguments of the spherical harmonics are given in the body system, but because $\underline{\kappa}$, the neutron momentum transfer, is fixed in the laboratory a rotation must be performed

$$Y^{k}_{\ell}(\hat{\underline{\kappa}}') = \sum_{m} D^{\ell}_{m,k}(\phi\theta\varphi)\,Y^{m}_{\ell}(\hat{\underline{\kappa}}). \qquad (3.25)$$

Now choosing the space - z axis to be along $\underline{\kappa}$ so that $Y^m_\ell(\hat{\underline{\kappa}})$ = $\delta_{mo}\sqrt{(2\ell + 1)/4\pi}$, we want to calculate

$$I_{\alpha'} I_{\alpha}^{*} = \sum_{\ell\ell' kk'} i^{\ell}(-i)^{\ell'} j_{\ell'}(\kappa b_{\alpha'}) j_{\ell}(\kappa b_{\alpha}) Y_{\ell'}^{k'}(\hat{b}_{\alpha'}) Y_{\ell}^{k*}(\hat{b}_{\alpha})$$

$$(\times)\sqrt{(2\ell+1)(2\ell'+1)}\,\langle JKM|D^{\ell'}_{0,k'}|JK'M'\rangle\langle JK'M'|D^{\ell *}_{0,k}|JKM\rangle . \qquad (3.26)$$

Explicitly, we want

$$\langle JKM|D^{\ell'}_{0,k'}|J'K'M'\rangle = \frac{1}{8\pi^2}\sqrt{(2J+1)(2J'+1)}\int d\Omega\, D^{J*}_{-M,-K} D^{\ell'}_{0,k'} D^{J'}_{-M',-K'}$$

$$\langle J'K'M'|D^{\ell *}_{0,k}|JKM\rangle = \frac{(-1)^{k}\sqrt{(2J+1)(2J'+1)}}{8\pi^2}\int d\Omega\, D^{J'*}_{-M',-K'} D^{\ell}_{0,-k} D^{J}_{-M,-K} \qquad (3.27)$$

We note that use of the Clebsch-Gordan series allows us to write

$$D^{j_1}_{\mu_1 m_1} D^{j_2}_{\mu_2 m_2} = \sum_{j=|j_2-j_1|}^{j_2+j_1} (-1)^{2(j_2-j_1)-(m_1+m_2+\mu_1+\mu_2)}(2j+1)$$

$$(\times)\begin{pmatrix} j_1 & j_2 & j \\ \mu_1 & \mu_2 & \mu_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m_3 \end{pmatrix} D^{j}_{\mu_1+\mu_2, m_1+m_2} , \qquad (3.28)$$

written here in terms of 3-j symbols, which are slightly symmetrized coefficients related to the Clebsch-Gordan coefficients by

$$C^{j_1\ j_2\ j_3}_{m_1\ m_2\ m_1+m_2} = (2j_3+1)^{1/2}(-1)^{-j_1+j_2-m_1-m_2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_1-m_2 \end{pmatrix} . \qquad (3.29)$$

Although not matrix elements of a unitary transformation as are the Clebsch-Gordan coefficients, the advantage of the 3-j symbols in tabulation is indisputable. Their high symmetry allows a tremendous abbreviation in the length of the table, with none of the concomitant hardship in finding the required particular symbol. The tables of Rotenberg, et al.,[64] for the 3-j symbols up to any integral angular momentum whose magnitude is less than or equal to 8 units are the most extensive tables to date. Then using the orthogonality integral

$$\int d\Omega\, D^{j_1 *}_{\mu_1 m_1} D^{j_2}_{\mu_2 m_2} = \frac{8\pi^2}{2j_1+1}\delta_{\mu_1\mu_2}\delta_{m_1 m_2}\delta_{j_1 j_2}, \tag{3.30}$$

the integral of three rotation matrices is given by

$$\int d\Omega\, D^{j_3 *}_{\mu_3 m_3} D^{j_2}_{\mu_2 m_2} D^{j_1}_{\mu_1 m_1} = 8\pi^2 \delta_{\mu_1+\mu_2,\mu_3}\delta_{m_1+m_2,m_3}(-1)^{2(j_2-j_1)-(m_1+m_2+\mu_1+\mu_2)} \times \begin{pmatrix} j_1 & j_2 & j_3 \\ \mu_1 & \mu_2 & -\mu_1-\mu_2 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_1-m_2 \end{pmatrix}. \tag{3.31}$$

Using (3.31) in (3.27), we find

$$\langle JKM | D^{\ell'}_{0,\kappa'} | J'K'M' \rangle = \sqrt{(2J+1)(2J'+1)}\,(-1)^{M+K'} \begin{pmatrix} J & J' & \ell' \\ M & -M' & 0 \end{pmatrix}\begin{pmatrix} J & J' & \ell' \\ K & -K' & K'-K \end{pmatrix}\delta_{K'-K,\kappa'} \tag{3.32}$$

$$\langle JKM | D^{\ell *}_{0,\kappa} | JKM \rangle = \sqrt{(2J+1)(2J'+1)}\,(-1)^{M+K'} \begin{pmatrix} J & J' & \ell' \\ M & -M' & 0 \end{pmatrix}\begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}\delta_{K'-K,\kappa}.$$

Now since the energy eigenvalues of the symmetric molecule are degenerate with respect to M and the sign of K, these matrix elements in (3.32) should be averaged over K,-K and the 2J+1 values of M. This corresponds to an orientational averaging process. Noting that summation over M and M' gives

$$\sum_{MM'} \begin{pmatrix} J & J' & \ell \\ M & -M' & 0 \end{pmatrix}\begin{pmatrix} J & J' & \ell' \\ M & -M' & 0 \end{pmatrix} = \delta_{\ell\ell'}/2\ell+1, \tag{3.33}$$

we have

$$I_{\alpha'} I^{*}_{\alpha} = 2\pi \sum_{J'} (2J'+1) \sum_{K,K',\ell} Q^{\alpha\alpha'}_{\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2, \tag{3.34}$$

where

$$Q^{\alpha\alpha'}_{\ell,K'-K} = j_\ell(\kappa b_{\alpha'})\, j_\ell(\kappa b_\alpha)\, Y_\ell^{K'-K}(\hat{\underline{b}}_{\alpha'})\, Y_\ell^{K'-K *}(\hat{\underline{b}}_{\alpha}). \tag{3.35}$$

The thermal average can be found immediately to be

$$\langle \chi_{\alpha\alpha'} \rangle_T = \frac{2\pi}{Z} \sum_{JJ'} (2J'+1) \sum_{K,K',\ell} Q^{\alpha\alpha'}_{\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2 e^{-\beta E_{JK}}, \tag{3.36}$$

where E_{JK} is given by (3.16) and the canonical ensemble partition function ($\beta = 1/k_BT$):

$$Z = \sum_{JK} e^{-\beta E_{JK}}. \tag{3.37}$$

The scattering of slow neutrons by the molecules in a gas or normal liquid may induce large numbers of different rotational transitions among the molecules, particularly when the neutron energies are larger than the rotational level spacings. In such cases for symmetric molecules, the work required to compute the cross section by direct summation using (3.36) is enormous due to the number of 3-j symbols which must be computed. It has been attempted with high-speed digital computers only for NH_3 at four energies,[65] although equivalent scattering law calculations have been reported by Strong, Harker, and Brugger.[66] Comparison of these results with experiment plus those for the numerically simpler linear or spherical molecules[67] indicate that at least for low momentum transfers (small energy and angle) the quantum description of rotations must be used in preference to the quasi-classical approximations of Krieger-Nelkin. It is this fact which has motivated our quantum treatment. Kosaly and Solt[68,69] have discussed the applicability of the Krieger-Nelkin treatment.

We will see that the computational difficulty the quantum treatment presents will again be present when internal rotation in the presence of free over-all rotation is discussed. There however, the simpler cases do not exist, in general, since linear and spherical molecules do not exhibit internal rotation.

3.3 ROTATIONAL HAMILTONIAN WITH INTERNAL ROTATION

In order to understand the problem of internal rotation and study its effects, the approximate Hamiltonian of the rotating system must be known. Since the origin of the potential barrier is not clearly understood, the only requirement that can be imposed on the potential function is that it be periodic in the relative angle α between the two parts of the molecule. Between $\alpha = 0$ and $\alpha = 2\pi$, the potential function must repeat itself N_f times, where N_f is the number of equivalent configurations in one complete internal revolution. In most cases the symmetry of the molecule is such that the potential function can be expressed as an even function of the angle α. The potential energy can then be expanded in a cosine series

$$V(\alpha) = \sum_k C_k \cos kN_f\alpha . \tag{3.38}$$

For the case of a threefold barrier, a shift in the reference level allows us to write

$$V(\alpha) = \frac{V_3}{2}(1-\cos 3\alpha) + \frac{V_6}{2}(1-\cos 6\alpha) + \cdots , \tag{3.39}$$

Since the ratio V_6/V_3 is commonly of the order of one-hundredth[70-72] or less we may take the potential function as simply

$$V(\alpha) = \frac{V_3}{2}(1-\cos 3\alpha). \tag{3.40}$$

The use of this simple potential function leads to solutions for the torsional wave equation in terms of solutions to the Mathieu equation.

In order to derive the kinetic energy, a model is used which consists of two rigid groups connected by a chemical bond. At least one of these groups is a symmetric top. For convenience, the symmetric top group is designated the internal rotor or top and is regarded as rotating internally about the bond with respect to the other group which is designated the frame or framework even if it is also a symmetric group. The entire molecule is also rotating. This over-all rotation will be treated first as free, but in later work we will discuss hindered over-all rotation as occurs in polar liquids.[73] For free over-all rotation and the internal rotation there are four degrees of freedom: the three Euler angles ψ, θ, φ of the framework and the relative angle α between the two groups. The method of solution is dictated by the functional form of the Hamiltonian which depends on the coordinate axes used. Two methods, the principal axes method[43,74] (hereafter referred to as the PAM) and the internal axis method [75-77] (hereafter referred to as the IAM) have been developed.

It is helpful in considering this problem to visualize four coordinate axis systems in each method. These four systems are: the space-fixed axis system (fixed in the laboratory); the internal rotation coordinate system (fixed somehow to the molecule as a whole); the top-fixed axis system; and the frame-fixed axis system.

Since the rotating top possesses an axis of symmetry, the principal axes of the whole molecule are not altered by a change of the relative orientation of the top and the frame. Hence, the principal axes coordinate system is regarded as rigidly attached to the frame in the PAM. However, in the IAM the axis about which the top executes internal rotation is chosen as one of the coordinate axes, the other two axes being fixed with respect to the frame with their orientation being, in principle, arbitrary but usually determined to some extent by the symmetry of the molecule.

3.3.1 Internal Axis Method

The case of a symmetric molecule will be treated first, and then an asymmetric molecule with a plane of symmetry will be treated by the IAM. References to other types of molecules will be given.

For symmetric molecules, a set of coordinate axes (x,y,z) is chosen with z axis along the symmetry axis of the molecule through the center of mass.[75,76] Then x and y axes can be fixed arbitrarily with respect to the frame because of its symmetric nature. The kinetic energy T can then be written (see Appendix G)

$$T = \frac{1}{2}\sum_{\ell k} I_{\ell k}\omega'_\ell \omega'_k + \frac{1}{2} I_a \dot{\alpha}^2 + I_a \omega'_z \dot{\alpha}, \tag{3.41}$$

$$= \frac{1}{2} I_x \omega'^2_x + \frac{1}{2} I_y \omega'^2_y + \frac{1}{2}(I_z - I_a)\omega'^2_z + \frac{1}{2} I_a (\omega'_z + \dot{\alpha})^2,$$

where $I_{\ell k}$ is the ℓkth element of the inertia tensor, I_x, I_y, and I_z are the three moments of inertia ($I_x=I_y=I$) of the whole molecule about the three coordinate axes, I_a is the moment of inertia of the rotor about its axis of symmetry (the z axis), ω'_x, ω'_y, ω'_z are the three components of the angular velocity of the molecule relative to the frame. Introducing the momenta

$$L'_x \equiv \frac{\partial T}{\partial \omega'_x} = I_x \omega'_x , \quad L'_z \equiv \frac{\partial T}{\partial \omega'_z} = I_z \omega'_z + I_a \dot{\alpha},$$
$$L'_y \equiv \frac{\partial T}{\partial \omega'_y} = I_y \omega'_y , \quad L'_a \equiv \frac{\partial T}{\partial \dot{\alpha}} = I_a(\omega'_z + \dot{\alpha}), \tag{3.42}$$

results in the Hamiltonian

$$H = \frac{L'^2_x}{2I_x} + \frac{L'^2_y}{2I_y} + \frac{L'^2_z}{2(I_z - I_a)} - \frac{L'_z L'_a}{(I_z - I_a)} + \frac{I_z L'^2_a}{2I_a(I_z - I_a)} + V(\alpha), \tag{3.43}$$

where as is shown in Appendix H, L'_x, L'_y, L'_z are the frame components of the total angular momentum (including internal rotation), and hence satisfy the usual anti-commutation relations of "body" system angular momentum operators.[56] L'_a is the total angular momentum of the rotor group including both the external and internal rotation, and commutes with L'_x, L'_y, and L'_z.

By applying the Nielsen transformation,[75]

$$L^i_a = L'_a - \frac{I_a}{I_z} L'_z = \left(1 - \frac{I_a}{I_z}\right) I_a \dot{\alpha} = r I_a \dot{\alpha} \tag{3.44}$$

which eliminates the cross product term $L'_a\ L'_z$ and where the reducing factor is

$$r = (I_z - I_a)/I_z , \tag{3.45}$$

(3.43) becomes

$$H = \frac{L'^2_x}{2I_x} + \frac{L'^2_y}{2I_y} + \frac{L'^2_z}{2I_z} + \frac{I_z L^{i\,2}_a}{2I_a(I_z - I_a)} + V(\alpha). \tag{3.46}$$

Unlike (3.43), the coefficients of the L's in (3.46) are the actual rotational constants of the <u>entire</u> molecule, and since L_a' commutes with $(L_x'^2 + L_y'^2)$, the Hamiltonian in (3.46) is separable into the over-all rotation and the internal rotation. However,

$$\left[L_a^i, L_x'\right] = i\hbar \frac{I_a}{I_z} L_y', \tag{3.47}$$

and also the matrix elements of L_x' and L_y' involve the quantum number associated with the torsional operator $\frac{I_z L_a^{i2}}{2I_a(I_z-I_a)} + V(\alpha)$. We may remove this dependence by a coordinate transformation.

The coordinate transformation corresponding to (3.44) is simply

$$\varphi' = \varphi + \frac{I_a}{I_z}\alpha = \frac{I_a\varphi_1 + (I_z-I_a)\varphi}{I_z}, \tag{3.48}$$

where $\varphi_1 = \varphi + \alpha$ is the third Euler angle of the rotor or top. One may regard ψ θ φ' as the Euler angles of a new set of axes. This coordinate system, called the "internal rotation coordinate system," is rotating with respect to the one attached to the frame with an angular velocity of $(I_a/I_z)\dot{\alpha}$ about the axis of symmetry of the molecule, so that to an observer in this system both the frame and the rotor appear to be moving. In this system the z component of the angular momentum due to internal rotation is zero.

Denoting the three components of the total angular momentum in the internal rotation coordinate system by L_x^i, L_y^i, and L_z^i, it follows that

$$\begin{aligned} L_x^i &= L_x' \cos \rho\alpha + L_y' \sin \rho\alpha, \\ L_y^i &= L_y' \cos \rho\alpha - L_x' \sin \rho\alpha, \\ L_z^i &= L_z', \end{aligned} \tag{3.49}$$

where

$$\rho = I_a / I_z \, . \tag{3.50}$$

Using (3.49) in (3.46) gives

$$H = \frac{L_x^{i\,2}}{2I_x} + \frac{L_y^{i\,2}}{2I_y} + \frac{L_z^{i\,2}}{2I_z} + \frac{I_z L_a^{i\,2}}{2I_a(I_z - I_a)} + V(\alpha), \tag{3.51}$$

which is the desired result, since L_x^i and L_y^i now commute with L_a^i and hence their matrix elements are independent of the torsional quantum number.

For an asymmetric molecule with a plane of symmetry, a set of coordinate axes is chosen similar to the symmetric molecule case with the z axis through the center of mass of the whole molecule and parallel to the symmetric internal rotor axis, and the y axis through the center of mass and lying in the plane of symmetry.[77-81] The inertial tensor has the form

$$\begin{bmatrix} I_x & 0 & 0 \\ 0 & I_y & -I_{yz} \\ 0 & -I_{yz} & I_z \end{bmatrix}$$

where I_{yz} is the product of inertia. Then from equation (3.41) the kinetic energy can be written as

$$T = \tfrac{1}{2} I_x \omega_x'^2 + \tfrac{1}{2} I_y \omega_y'^2 + \tfrac{1}{2} I_z \omega_z'^2 - I_{yz} \omega_y' \omega_z' + \tfrac{1}{2} I_a \dot{\alpha}^2 + I_a \omega_z' \dot{\alpha} \tag{3.52}$$

Similarly defining the momenta

$$
\begin{aligned}
L'_x &\equiv \partial T/\partial \omega'_x = I_x \omega'_x, \\
L'_y &\equiv \partial T/\partial \omega'_y = I_y \omega'_y - I_{yz} \omega'_z, \\
L'_z &\equiv \partial T/\partial \omega'_z = I_z \omega'_z - I_{yz} \omega'_y + I_a \dot{\alpha}, \\
L'_a &\equiv \partial T/\partial \dot{\alpha} = I_a(\dot{\alpha} + \omega'_z),
\end{aligned}
\qquad (3.53)
$$

Substituting (3.53) into (3.52) the Hamiltonian becomes

$$
\begin{aligned}
H = {} & A L'^2_x + B L'^2_y + C L'^2_z + D(L'_y L'_z + L'_z L'_y) \\
& - 2D L'_y L'_a - 2C L'_z L'_a + F L'^2_a + V(\alpha),
\end{aligned}
\qquad (3.54)
$$

where

$$
\begin{aligned}
A &= \hbar^2/2I_x, & F &= \hbar^2/2rI_a, \\
B &= (I_z - I_a)\hbar^2/2d, & r &= \frac{I_y I_z - I_y I_a - I_{yz}^2}{I_y I_z - I_{yz}^2}, \\
C &= I_y \hbar^2/2d, & & \\
D &= I_{yz} \hbar^2/2d, & d &= I_y I_z - I_y I_a - I_{yz}^2.
\end{aligned}
\qquad (3.55)
$$

We now apply three transformations to the Hamiltonian given in (3.54), rather than follow the method used in the symmetric case. Although the coupling between L'_a and L'_z can be eliminated in the symmetric case by a Nielsen transformation, it would not be removed completely for the asymmetric molecule but would be reduced by a factor $I_{yz}^2/I_y I_z$. However, in order to minimize the coupling term the z component of the internal angular momentum must be made to vanish. This can be accomplished with the following transformations. First, a rotation is performed in order to eliminate the $L'_y\ L'_a$ coupling. Second, a modified Nielsen transformation is used to eliminate the $L'_z L'_a$ coupling. Third, we transform into the internal rotation coordinate system. The first two are accomplished with the following:

$$
\begin{aligned}
L''_x &= L'_x , \\
L''_y &= (I_y L'_y - I_{yz} L'_z)/(I_y^2 + I_{yz}^2)^{1/2} , \\
L''_z &= (I_{yz} L'_y + I_y L'_z)/(I_y^2 + I_{yz}^2)^{1/2} , \\
L''_a &= L'_a - L''_z I_a (I_y^2 + I_{yz}^2)^{1/2} (I_y I_z - I_{yz}^2)^{-1} .
\end{aligned}
\tag{3.56}
$$

The transformed Hamiltonian which results from these two operations is

$$
\begin{aligned}
H = {} & A L''^2_x + B'' L''^2_y + C'' L''^2_z + D''(L''_y L''_z + L''_z L''_y) \\
& + F L''^2_a + V(\alpha) ,
\end{aligned}
\tag{3.57}
$$

where

$$
B'' = \frac{\hbar^2 I_y}{2(I_y^2 + I_{yz}^2)} , \quad C'' = \frac{\hbar^2}{2}\left[\frac{I_y + I_z}{I_y I_z - I_{yz}^2}\right] - B'' , \quad D'' = \frac{\hbar^2 I_{yz}}{2(I_y^2 + I_{yz}^2)} .
\tag{3.58}
$$

Now using the transformation described by (3.49) on the quantities in (3.57) with ρ given by (3.60), the resulting Hamiltonian referred to the internal rotational axes, where the z component of the internal angular momentum vanishes, is

$$
\begin{aligned}
H = {} & \tfrac{1}{2}(A + B'')(L^{i2}_x + L^{i2}_y) + C'' L^{i2}_z + F L^{i2}_a + V(\alpha) \\
& + \tfrac{1}{2}(A - B'')\left[(L^{i2}_x - L^{i2}_y)\cos 2\rho\alpha - (L^i_x L^i_y + L^i_y L^i_x)\sin 2\rho\alpha\right] \\
& + D''\left[(L^i_y L^i_z + L^i_z L^i_y)\cos \rho\alpha + (L^i_x L^i_z + L^i_z L^i_x)\sin \rho\alpha\right] ,
\end{aligned}
\tag{3.59}
$$

where

$$\rho = \frac{(I_y^2 + I_{yz}^2)^{1/2} I_a}{I_y I_z - I_{yz}^2}, \tag{3.60}$$

It can easily be shown that L_x^i, L_y^i, and L_z^i satisfy the usual anticommutation rules

$$[L_i^i, L_j^i] = -i\hbar L_k^i, \qquad i,j,k = x,y,z \text{ in cyclic order}$$
$$[L_a^i, L_i^i] = 0. \tag{3.61}$$

Finally, two other types of molecular symmetry have been considered in the literature. For molecules with two perpendicular planes of symmetry the above formulas apply with $I_{yz} = 0$.[82-84] For molecules with no planes of symmetry the method is similar to that outlined above.[78,85]

3.3.2 Principal Axes Method

In the PAM the symmetric molecule Hamiltonian is given by (3.43) with principal axes coincident with those of the IAM. However, the Nielsen transformation is not applied. For an asymmetric molecule in the PAM, the coordinates are chosen as the principal axes of the entire molecule and are fixed in the frame. The orientation of the principal axes relative to the frame is not altered by the rotation of the rotor due to its cylindrical symmetry. The kinetic energy, from (3.41), is

$$T = \tfrac{1}{2} I_x \omega_x'^2 + \tfrac{1}{2} I_y \omega_y'^2 + \tfrac{1}{2} I_z \omega_z'^2 + I_a \lambda_x \omega_x' \dot{\alpha} + I_a \lambda_y \omega_y' \dot{\alpha} + I_a \lambda_z \omega_z' \dot{\alpha} + \tfrac{1}{2} I_a \dot{\alpha}^2, \tag{3.62}$$

where λ_x, λ_y, and λ_z are the direction cosines of the symmetry axis of the rotor to the principal axes. Defining the momenta as before, the Hamiltonian becomes

$$H = A_x L_x'^2 + B_y L_y'^2 + C_z L_z'^2 + F L_a'^2 + V(\alpha) + \frac{1}{2}\sum_{i,j}{}' D_{ij}(L_i' L_j' + L_j' L_i') - 2\sum_i Q_i L_i' L_a', \qquad (3.63)$$

where

$$A_x = \frac{\hbar^2}{2I_x}\left[1 + \frac{\lambda_x^2 I_a}{r I_x}\right], \qquad (3.64)$$

and similarly for B_y and C_z by the permutation (x,y,z),

$$D_{ij} = \frac{\hbar^2 \lambda_i \lambda_j I_a}{2r I_i I_j}, \qquad F = \frac{\hbar^2}{2r I_a},$$
$$Q_i = \frac{\lambda_i \hbar^2}{2r I_i}, \quad r = 1 - \frac{\lambda_y^2 I_a}{I_y} - \frac{\lambda_z^2 I_a}{I_z}. \qquad (3.65)$$

For molecules with a plane of symmetry in their frame, the above applies with $\lambda_x = 0$ (or $\lambda_y = 0$).[70,86] With two planes of symmetry both of the direction cosines are set to zero.[82]

3.4 HIGH- AND LOW-BARRIER APPROXIMATIONS

The Hamiltonians derived above can generally be divided into an overall rotational part, an internal rotation torsional part, and a coupling between them. Since the separation is not complete, except in the case of a symmetric molecule, the Schroedinger equation cannot be solved exactly and hence perturbation theory is usually applied. For analysis of neutron scattering we will see that this may limit the useful description to nearly symmetric molecules.

One of two approaches can be applied depending upon the barrier height. The high-barrier approximations are applicable to the cases where the separations of the torsional energy levels are large compared with the over-all rotational energy separations. In the low-barrier approximations discussed later, the problem of the free internal rotor is solved first and then the barrier may be treated as a perturbation.

The Schroedinger equation for a high barrier (> .06 ev) can be solved by using either the PAM or IAM. In the discussion which follows, the symmetric molecule is treated first by both the PAM and IAM. Then the effect of asymmetry of the molecular frame is introduced into both the PAM and IAM. Finally, the low-barrier case is discussed.

3.4.1 High Barriers

In the PAM, the Hamiltonian for symmetric molecules ($I_x=I_y=I$) was written as

$$H_R = H_{SR} + H_T + H_P, \tag{3.66}$$

where now

$$\begin{aligned} &H_{SR} = A(L_x'^2 + L_y'^2) + C'L_z'^2, \quad H_T = FL_\alpha'^2 + V(\alpha), \\ &H_P = -2C'L_z'L_\alpha', \qquad A = \hbar^2/2I, \\ &C' = \hbar^2/2(I_z - I_\alpha), \quad F = \frac{\hbar^2 I_z}{2I_\alpha(I_z - I_\alpha)}. \end{aligned} \tag{3.67}$$

We shall first consider a perturbation solution approach. It will be seen that this perturbation approach is not convenient for the description of neutron scattering due to the fact that determination of the energy levels and wave functions requires substantial numerical work. However, in the IAM the wave functions can, in principle, be obtained exactly.

Proceeding with the PAM perturbation solution, the energy matrix is constructed in a representation in which the over-all rotation part H_{SR} and the internal torsion part H_T are separately diagonal. H_P, consisting of the cross terms between the total angular momentum and the internal angular momentum, is chosen as the perturbation. The basis functions are then the product of the rigid symmetric top wave functions and the torsional functions which are related to the tabulated Mathieu functions. The perturbation terms are treated by the Van Vleck transformation,[87] so that after this transformation the secular equation can be approximately factored into blocks corresponding to different torsional states. Since H_P does not vanish at the limit of an infinite barrier, the effect of the perturbation is not small. Consequently, for molecules with an intermediate barrier, fourth-order perturbation procedure must be used.

The rigid symmetric top wave functions are the eigenfunctions of H_{SR} and were expressed before as [62,63]

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^{J}_{-M,-K}(\psi\theta\varphi), \qquad (3.68)$$

where the factored dependence on the Euler angles is given by (3.21).

The eigenvalues associated with (3.68) and hence H_R are

$$E_{JKM} = AJ(J+1) + (C'-A)K^2. \qquad (3.69)$$

In order to find the torsional eigenfunctions and eigenvalues, we must solve

$$\left[-F\frac{d^2}{d\alpha^2}+V(\alpha)\right]U(\alpha)=E\,U(\alpha), \tag{3.70}$$

with V(α) given by (3.40). Letting

$$\begin{aligned} &3\alpha+\pi=2x, && s=4V_3/9F, \\ &U[(3\alpha+\pi)/2]=M(x), && b=4E/9F, \end{aligned} \tag{3.71}$$

we obtain from (3.70) the Mathieu equation

$$\frac{d^2M(x)}{dx^2}+\left[\left(b-\frac{s}{2}\right)-\frac{s}{2}\cos 2x\right]M(x)=0, \tag{3.72}$$

whose solutions must be periodic in 2π and hence can be expanded in Fourier series. This procedure leads to an infinite set of secular equations from which the eigenvalues can be found in a systematic fashion and the Fourier coefficients of the eigenfunctions are then obtainable from the recursion relations associated with the infinite order determinantal equations.[88] However, we still must treat the perturbation terms in the PAM. The energy matrix is now grouped into blocks along the diagonal, the Hamiltonian within each block being $H_{SR}+H_T$, and blocks of different torsional quantum number are connected by the matrix elements of H_P. The Van Vleck transformation effectively folds the nondiagonal elements onto the blocks and can be applied successively to yield nth order perturbation calculations[88] when the energy separations between different torsional states are large compared to those between rotational levels of the same torsional quantum number. But, this is more numerical calculation. Instead, we turn to the IAM.

The essential feature of the IAM is the application of the Nielsen transformation to remove the coupling term between over-all and internal rotation. We will use this to advantage. The Hamiltonian for symmetric molecules in the IAM was given as

$$H_R = A(L_x^{i\,2} + L_y^{i\,2}) + C L_z^{i\,2} + F L_\alpha^{i\,2} + V(\alpha), \tag{3.73}$$

where $C = h^2/2I_z$. Since L_x^i, L_y^i, L_z^i do not contain α (see Appendix H) the wave function can be written as a product

$$\Xi(\psi\theta\varphi'\alpha) = D^J_{-M,-K}(\psi\theta\varphi')\,M(\alpha), \tag{3.74}$$

where

$$\begin{aligned} L^{i\,2} D^J_{-M,-K}(\psi\theta\varphi') &= \hbar^2 J(J+1) D^J_{-M,-K}(\psi\theta\varphi'), \\ L_3 D^J_{-M,-K}(\psi\theta\varphi') &= \hbar M D^J_{-M,-K}(\psi\theta\varphi'), \\ L_3^i D^J_{-M,-K}(\psi\theta\varphi') &= \hbar K D^J_{-M,-K}(\psi\theta\varphi'), \end{aligned} \tag{3.75}$$

such that K is now interpretable as the projection of J on the internal rotation z axis which is coincident with the top and frame z axes, and where $M(\alpha)$ is the solution of

$$\left[-F\frac{d^2}{d\alpha^2} + \frac{V_3}{2}(1-\cos 3\alpha)\right]M(\alpha) = E\,M(\alpha), \tag{3.76}$$

with the appropriate boundary conditions, and the eigenvalues of (3.73) are

$$E_{JKM} + E = AJ(J+1) + (C-A)K^2 + E. \tag{3.77}$$

By application of Floquet's theorem[89] the solutions of Mathieu's equation (3.76) can be written as the product of two functions

$$M(\alpha) = e^{if\alpha} P(\alpha), \tag{3.78}$$

where $P(\alpha)$ is periodic in 2π and f is to be determined from the boundary conditions. The necessary and sufficient condition for single-valuedness of the wave function in φ' and α is

$$\Xi\left\{\psi, \theta, \varphi' + \frac{2\pi}{I_z}\left[I_a i_1 + (I_z - I_a) i_2\right], \alpha + 2\pi(i_2 - i_1)\right\} = \Xi\left\{\psi, \theta, \varphi', \alpha\right\}, \tag{3.79}$$

where i_1 and i_2 are integers. Single-valuedness of the wave function while commonly imposed as a boundary condition here is not a completely valid requirement. Only observable quantities are required to be single-valued. Nevertheless we impose (3.79), which means that

$$e^{iK\varphi'} e^{if\alpha} P(\alpha) = e^{iK\varphi'} e^{if\alpha} P(\alpha) \times e^{2\pi i\alpha\left\{\frac{K}{I_z}\left[I_a i_2 + (I_z - I_a) i_1\right] + f(i_2 - i_1)\right\}}. \tag{3.80}$$

Thus

$$\frac{K}{I_z}\left[I_a i_2 + (I_z - I_a) i_1\right] + f(i_2 - i_1) = i_3, \tag{3.81}$$

where i_3 is an integer. This can be satisfied by setting f equal to either $-\frac{I_a}{I_z}K$ or $\frac{I_z - I_a}{I_z}K$. It is convenient to take $f = -\frac{I_a}{I_z}K$ so that the torsional wave function becomes

$$M(\alpha) = P(\alpha) e^{-iK\frac{I_a}{I_z}\alpha}, \tag{3.82}$$

and its boundary condition becomes

$$M(\alpha+2\pi) = M(\alpha) e^{-2\pi i K\frac{I_a}{I_z}}. \tag{3.83}$$

This boundary condition demands general quasi-periodic solutions of (3.76) which can be obtained by the method of continued fractions.[78] The wave functions are then general Mathieu functions. In principle, we can employ these wave functions to find the matrix elements required for the description of the neutron scattering cross section. However, we will see that in the case of high internal barriers it is advantageous to approximate the required matrix elements through use of approximate but simple wave functions. The eigenvalues and wavefunctions of (3.76) are threefold degenerate. We will denote the solutions by $U_{n,\delta}(\alpha)$ where n is the torsional quantum number and $\delta = 0, \pm 1$ labels the degenerate states.

The effect of asymmetry of the molecular frame which gives rise to the additional terms in the Hamiltonians (3.59) and (3.63) splits some of these degenerate levels so that the levels corresponding to $U_{n,o}$ become nondegenerate but the others remain doubly degenerate.[78] The determination of energies and wave functions for asymmetric molecules is complicated by the presence of the additional terms in the Hamiltonians, leading again to unsuitable numerical work for our purposes.

3.4.2 Low Barriers and Free Internal Rotation

For symmetric molecules with low enough barriers the free internal rotational problem can be solved exactly. Adding the barrier as a perturbation or treating the effect of asymmetry as a perturbation cannot be done without numerical work for either the PAM or IAM. Therefore, for symmetric molecules we write the Hamiltonian as

$$H_R = A\left(L_x^{i\,2} + L_y^{i\,2}\right) + C L_z^{i\,2} + F L_a^{i\,2} . \tag{3.84}$$

The eigenvalues and eigenfunctions for free internal rotation are easily found to be

$$\begin{aligned} E_{mJKM} &= AJ(J+1) + (C-A)K^2 + F\left[m - \frac{I_a}{I_z}K\right]^2 , \\ |mJKM\rangle &= \left(\frac{2J+1}{16\pi^3}\right)^{1/2} D^J_{M,-K}(\phi\theta\psi)\, e^{i\left[m - \frac{I_a}{I_z}K\right]\alpha} , \end{aligned} \tag{3.85}$$

where m is an integer. The energy is independent of the sign of $m - \frac{I_a}{I_z} K$, because if the direction of rotation of both the whole molecule and the internal motion is reversed E_{mJKM} must be invariant. Hence, each state $|mJKM>$ is 2(2J+1)-fold degenerate.

3.5 THE DIFFERENTIAL CROSS SECTIONS

Now having at our disposal the rotational Hamiltonians, rotational energy eigenvalues, and rotational wave functions appropriate to symmetrical molecules with an internal rotational degree of freedom undergoing free over-all rotation as occurs in gases or normal liquids, we will describe the neutron differential scattering cross section using the simple formalism which ignores line shift and width. We will confine our attention to the two limiting classes of internal rotation, since the specific class of hindered internal rotation requires extensive numerical work in specifying the wave functions with Fourier expansions or continued fractions.

Recalling from the rigid rotator discussion the computational problem involved in this approach of explicit summation of all the possible free over-all rotational transitions, it is clear that a formulation of the problem is appropriate in which these enormous numbers of closely spaced discrete transitions are approximately summed by integration. This is the philosophy of the Krieger-Nelkin quasi-classical approximation.[26] After deriving the quantum result, we will discuss a quasi-classical description which treats approximately certain quantities in the rigorous formulation.

3.5.1 Quantum Description

Recalling equations (2.26) and (2.27), we substitute j and σ for ℓ and α labels for convenience. We note that (2.27) requires a description of translation and vibration as well as rotation. Letting the translational motion be free as in a gas, we have

$$\langle \chi_{jj'} \rangle_T = e^{-\left(i\frac{t}{\hbar}\frac{\hbar^2\kappa^2}{2M} + \frac{t^2}{\hbar^2\beta}\frac{\hbar^2\kappa^2}{2M}\right)} \sum_{\sigma\sigma'} a_{j\sigma} a_{j'\sigma'} \langle \chi^{I}_{j\sigma j'\sigma'} \rangle_T , \tag{3.86}$$

where the first factor is the translational thermal average for free molecules of mass M with $\beta = 1/k_BT$, which may be replaced in the case of a normal liquid by a more appropriate description of the translational degrees of freedom, and where the last factor is

$$\left\langle \chi^{I}_{jj'\sigma\sigma'} \right\rangle_T = \sum_{\text{rot. states}} P_{rot} \left\langle \Psi_{rot} \right| e^{i\underline{\kappa}\cdot \underline{b}_{j\sigma}(t)} V'_{\sigma\sigma'} e^{-i\underline{\kappa}\cdot \underline{b}_{j'\sigma'}} \left| \Psi_{rot} \right\rangle, \tag{3.87}$$

with

$$V'_{\sigma\sigma'} = \sum_{\text{vib. states}} P_{vib} \left\langle \Psi_{vib} \right| e^{i\underline{\kappa}\cdot \sum_\lambda \underline{C}^\lambda_\sigma(t) q_\lambda(t)} e^{-i\underline{\kappa}\cdot \sum_\lambda \underline{C}^\lambda_{\sigma'} q_\lambda} \left| \Psi_{vib} \right\rangle. \tag{3.88}$$

The vibrational and rotational thermal averages are not separable due to the noncommutativity of H_R and $\underline{C}_\sigma$, which accounts for the rotation of the axes of vibration during a neutron scattering event.

The vibrational thermal average for a collection of oscillators is[11]

$$\begin{aligned} V'_{\sigma\sigma'} = \prod_\lambda \sum_{n_\lambda} & e^{n_\lambda \hbar\omega_\lambda \left(i\frac{t}{\hbar} - \frac{\beta}{2}\right)} e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\underline{\kappa}\cdot \underline{C}^\lambda_\sigma(t)\right]^2 \coth\frac{\beta}{2}\hbar\omega_\lambda} \\ & \times I_{n_\lambda}\left(\frac{\hbar(\underline{\kappa}\cdot\underline{C}^\lambda_\sigma(t))(\underline{\kappa}\cdot\underline{C}^\lambda_{\sigma'})}{2M_\lambda\omega_\lambda \sinh(\frac{\beta}{2}\hbar\omega_\lambda)}\right) e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\underline{\kappa}\cdot\underline{C}^\lambda_{\sigma'}\right]^2 \coth\frac{\beta}{2}\hbar\omega_\lambda} . \end{aligned} \tag{3.89}$$

If we restrict consideration to neutron energies below the vibrational threshold (lowest vibrational energy), assume that all molecules are initially in their ground states, and assume that $\frac{\beta\hbar\omega_\lambda}{2} >> 1$, then this reduces to the form

$$V'_{\sigma\sigma'}=\prod_{\lambda} e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma}(t)\right]^2} e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma'}\right]^2} . \tag{3.90}$$

The time dependence of $\underline{C}^{\lambda}_{\sigma}(t)$ may be explicitly displayed as

$$\begin{aligned}\underline{C}^{\lambda}_{\sigma}(t) &= e^{i\frac{t}{\hbar}H_R}\,\underline{C}^{\lambda}_{\sigma}\,e^{-i\frac{t}{\hbar}H_R} ,\\ &= \sum_{n=0}^{\infty}\frac{i^n t^n}{n!\,\hbar^n}\left[H_R,\underline{C}^{\lambda}_{\sigma}\right].\end{aligned}$$

Keeping terms through the first order commutator, (3.90) becomes

$$\begin{aligned}V'_{\sigma\sigma'} &= \prod_{\lambda} e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\left(\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma}+i\frac{t}{\hbar}\underline{\kappa}\cdot\left[H_R,\underline{C}^{\lambda}_{\sigma}\right]\right)^2\right]}\\ &\quad (\times)\, e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma'}\right]^2} .\end{aligned} \tag{3.91}$$

To write this as a single exponential of a sum of operators requires use of the full Baker-Hausdorff theorem on operator products [see Equation 3.123)]. However, considerable simpliciation occurs if we ignore the first order commutator as well as all higher order ones. Then, (3.91) reduces to the time-independent form

$$V'_{\sigma\sigma'}=\prod_{\lambda} e^{-\frac{\hbar}{4M_\lambda\omega_\lambda}\left[\left(\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma}\right)^2+\left(\underline{\kappa}\cdot\underline{C}^{\lambda}_{\sigma'}\right)^2\right]} . \tag{3.92}$$

Ignoring the commutator series is closely related to ignoring the change in the moments of inertia during a vibrational period which is a kind of rotation-vibration interaction.

The amplitude vectors $\underline{C}^{\lambda}$, like the vectors $\underline{b}$, are fixed in the frame or top and rotate with the molecule. The similarity of the $\underline{C}^{\lambda}$'s to rotator coordinates is seen in their failure to commute with the b's except when evaluated at equal times. It is for this reason that rotation and vibration effects cannot be rigorously separated from one another in the calculation of thermal averages as can be seen by substituting (3.90) or (3.92) into (3.87).

Nevertheless, we will assume that for our purposes we can ignore the nonseparability of rotational and vibrational thermal averages. According to Zemach and Glauber[9] this assumption corresponds to ignoring the effect of rotation of the axes of vibration during a scattering event. Then the thermal average is written as a product of thermal averages. In approximating the vibrational thermal average, we take the average of a function to be approximately the function of the average, and write

$$V'_{\sigma\sigma'} = e^{-\kappa^2 \gamma_{\sigma\sigma'}}, \tag{3.93}$$

where the vibrational constant

$$\gamma_{\sigma\sigma'} = \sum_{\lambda} \frac{\hbar}{12 M_\lambda \omega_\lambda} \left[(C_\sigma^\lambda)^2 + (C_{\sigma'}^\lambda)^2 \right], \tag{3.94}$$

is a parameter in this description.

We will now concentrate our attention on the rotational degrees of freedom. From the standpoint of energy transfer the case of interest is the scattering from a single molecule since "outer" scattering, interference scattering from different molecules, is necessarily elastic in the present description. Strictly for computational purposes, the sum over σ and σ' as labels of nuclei has been taken outside the matrix element leaving generic types of matrix elements to calculate and then sum. The scattering lengths then become the conventional appropriately averaged quantities. The various generic types of matrix elements will not be given names here, but the index g=1,2,3,4 will be used to differentiate between them. The first type (g=1) of matrix element involves the ordered pair in which the first nucleus is in the frame and the second nucleus is in the top, the second type (g=2) involves this ordered pair in reverse order, third type (g=3) involves both nuclei being in the top, and the last type (g=4) involves both nuclei being in the frame. For a molecule such as ethane, CH_3-CH_3, the interchange of frame and rotor systems, while changing one generic type into another, leaves the sum invariant.

Then for symmetric molecules all the types of matrix elements in the high internal barrier (or bound) case are of the form

$$\langle \sigma\sigma'; \delta n J K M\rangle = \langle \delta n J K M | e^{\frac{it}{\hbar} H_R} e^{i\underline{\kappa}\cdot \underline{b}_{\sigma}} e^{-\frac{it}{\hbar} H_R} e^{-i\underline{\kappa}\cdot \underline{b}_{\sigma'}} | \delta n J K M\rangle, \tag{3.95}$$

where we have suppressed j, the molecular label, and where

$$|\delta n J K M\rangle = N_{nJKM}\, D^{J}_{-M,-K}(\psi\theta\varphi')\, U_{n,\delta}(\alpha), \tag{3.96}$$

and $\delta = 0, \pm 1$ labels the threefold degenerate states for a given torsional quantum number n.

We can eliminate large numerical calculations in finding these matrix elements, if we take advantage of the fact that for high enough barriers the internal motion consists of small oscillations and hence find approximate wave functions. We will first consider oscillations about the potential energy minimum at $\alpha = 0$. By expanding the hindering potential in a Maclaurin series and neglecting higher order terms, we find

$$\frac{d^2M(\alpha)}{d\alpha^2} + (\delta + \xi^2\alpha^2)M(\alpha) = 0, \tag{3.97}$$

where

$$\delta = E_n/F, \quad \xi^2 = 9V_3/4F. \tag{3.98}$$

For small values of K the classical amplitude of the motion is such that the exponential in (3.82) will be essentially constant, and hence, inserting for the exponential its value at $\alpha = 0$, we have

$$M(\alpha) = P(\alpha), \tag{3.99}$$

and the energies and wave functions become

$$\begin{aligned} E_{nJKM} &= AJ(J+1) + (C-A)K^2 + \hbar\omega_T(n+\tfrac{1}{2}), \\ |nJKM\rangle &= N_{nJKM}\, D^J_{-M,-K}(\psi\theta\varphi')\, e^{-\frac{1}{2}\xi\alpha^2} H_n(\xi^{\frac{1}{2}}\alpha), \end{aligned} \tag{3.100}$$

where

$$\omega_T = 3\sqrt{V_3 F}/\hbar \tag{3.101}$$

and where H_n is the Hermite polynomial of the nth order. There will be two other internal states having this same energy; they are the states in which the system is executing an exactly similar vibration about the minima at $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$. The wave functions for the other two states will be as given above except the internal wave functions will be written in terms of the variables $\alpha + \frac{2k-2}{3}\pi$, $k = 2,3$ and will be multiplied by phase factors $e^{-\frac{2k-2}{3}\pi i \frac{I_a}{I_z} K}$.

When the tunneling effect is considered, the correct zeroth-order torsional functions for our hindering potential can be found from group theory and are[78]

$$\begin{aligned} U_{n,0}(\alpha) &= \frac{1}{\sqrt{3}}\left[M_n^{(1)} + M_n^{(2)} + M_n^{(3)}\right], \\ U_{n,1}(\alpha) &= \frac{1}{\sqrt{3}}\left[M_n^{(1)} + e^{\frac{2\pi i}{3}} M_n^{(2)} + e^{\frac{4\pi i}{3}} M_n^{(3)}\right], \\ U_{n,-1}(\alpha) &= \frac{1}{\sqrt{3}}\left[M_n^{(1)} + e^{\frac{4\pi i}{3}} M_n^{(2)} + e^{\frac{2\pi i}{3}} M_n^{(3)}\right], \end{aligned} \tag{3.102}$$

where

$$\begin{aligned} M_n^{(1)} &= e^{-\frac{1}{2}\xi\alpha^2} H_n(\xi^{\frac{1}{2}}\alpha), \\ M_n^{(2)} &= e^{-\frac{2\pi i}{3} K \frac{I_a}{I_z}} e^{-\frac{1}{2}\xi(\alpha + \frac{2\pi}{3})^2} H_n\left[\xi^{\frac{1}{2}}(\alpha + \tfrac{2\pi}{3})\right], \\ M_n^{(3)} &= e^{-\frac{4\pi i}{3} K \frac{I_a}{I_z}} e^{-\frac{1}{2}\xi(\alpha + \frac{4\pi}{3})^2} H_n\left[\xi^{\frac{1}{2}}(\alpha + \tfrac{4\pi}{3})\right]. \end{aligned} \tag{3.103}$$

The normalization factor N_{nJKM} is given by

$$N_{nJKM}^2 = \left(\frac{\xi}{\pi}\right)^{\frac{1}{2}} \frac{1}{2^n n!} \, \frac{2J+1}{8\pi^2} \,. \tag{3.104}$$

In the same way that it arises in the case of a rigid molecule, a useful expansion for the purpose of calculating the matrix elements is

$$e^{i\underline{\mathcal{K}}\cdot\underline{b}_\sigma} = 4\pi \sum_{\ell k} i^\ell j_\ell(\mathcal{K} b_\sigma) Y_\ell^{k*}(\hat{\underline{b}}_\sigma') Y_\ell^k(\hat{\underline{\mathcal{K}}}'), \tag{3.105}$$

when the σth atom is in the frame, j_ℓ is the ℓth order spherical Bessel function and the prime indicates that arguments of the spherical harmonics are measured with respect to the frame-fixed axes. Because $\underline{\mathcal{K}}$ is specified in the laboratory, a rotation yields

$$Y_\ell^k(\hat{\underline{\kappa}}') = \sum_m e^{-im\psi} d^\ell_{m,k}(\theta) e^{-ik\varphi} Y_\ell^m(\hat{\underline{\kappa}}) \qquad (3.106)$$

where $\underline{\kappa}$ has components in the space system. Making the substitution $\varphi = \varphi' - \rho\alpha$, allows the given rotation matrix whose variables are the Euler angles between frame-fixed and space-fixed axes to be expressed in terms of the Euler angles between the internal rotation axes and the space-fixed axes. We find for an atom in the frame

$$e^{i\underline{\kappa}\cdot\underline{b}_\sigma} = 4\pi \sum_{\ell k m} i^\ell j_\ell(\kappa b_\sigma) Y_\ell^{k*}(\hat{\underline{b}}_\sigma') Y_\ell^m(\hat{\underline{\kappa}}) D^\ell_{m,k}(\psi\theta\varphi') e^{ik\rho\alpha}. \qquad (3.107)$$

However, if the σth atom is in the top, we must expand

$$e^{i\underline{\kappa}\cdot\underline{b}_{\sigma'}} = 4\pi \sum_{\ell k} i^\ell j_\ell(\kappa b_{\sigma'}) Y_\ell^{k*}(\hat{\underline{b}}_{\sigma'}'') Y_\ell^k(\hat{\underline{\kappa}}''), \qquad (3.108)$$

where now the arguments of the spherical harmonics are measured with respect to the top-fixed axes. A rotation yields

$$Y_\ell^k(\hat{\underline{\kappa}}'') = \sum_\mu D^\ell_{\mu,k}(\alpha 0 0) Y_\ell^\mu(\hat{\underline{\kappa}}'), \qquad (3.109)$$

but we have $D^\ell_{\mu,k}(\alpha 00) = \delta_{k\mu} e^{-ik\alpha}$, so that

$$Y_\ell^k(\hat{\underline{\kappa}}'') = e^{-ik\alpha} Y_\ell^k(\hat{\underline{\kappa}}'). \qquad (3.110)$$

Hence,

$$Y_\ell^k(\hat{\underline{\kappa}}'') = \sum_m e^{-ik\alpha} D^\ell_{m,k}(\psi\theta\varphi) Y_\ell^m(\hat{\underline{\kappa}}), \qquad (3.111)$$

and again making the substitution $\varphi = \varphi' - \rho\alpha$, our expansion for an atom in the top finally becomes

$$e^{i\underline{\kappa}\cdot\underline{b}_{\sigma'}} = 4\pi\sum_{\ell k m} i^{\ell} j_{\ell}(\kappa b_{\sigma'}) Y_{\ell}^{k*}(\hat{\underline{b}}''_{\sigma'}) Y_{\ell}^{m}(\hat{\underline{\kappa}}) \\ (\times) D^{\ell}_{m,k}(\psi\theta\varphi') e^{-ik(1-\rho)\alpha} . \tag{3.112}$$

Choosing the space-z axis along $\underline{\kappa}$, $Y_{\ell}^{m}(\hat{\underline{\kappa}}) = \delta_{m0}\sqrt{(2\ell+1)/4\pi}$.

Using this last relation in both expansions (3.107) and (3.112), we have that

$$e^{i\underline{\kappa}\cdot\underline{b}_{\sigma}} = \sum_{\ell k}\sqrt{4\pi(2\ell+1)}\, i^{\ell} j_{\ell}(\kappa b_{\sigma}) Y_{\ell}^{k*}(\hat{\underline{b}}'_{\sigma}) D^{\ell}_{0,k}(\psi\theta\varphi') e^{ik\rho\alpha} ,$$
$$e^{i\underline{\kappa}\cdot\underline{b}_{\sigma'}} = \sum_{\ell k}\sqrt{4\pi(2\ell+1)}\, i^{\ell} j_{\ell}(\kappa b_{\sigma'}) Y_{\ell}^{k*}(\hat{\underline{b}}''_{\sigma'}) D^{\ell}_{0,k}(\psi\theta\varphi') e^{-ik(1-\rho)\alpha} . \tag{3.113}$$

Letting g=1,2,3,4 label the kinds of matrix elements and then restricting σ and σ' appropriately, we can write (3.95) as

$$\langle\sigma\sigma' ; \delta n J K M\rangle = \sum_{gJ'K'M'} e^{i\frac{t}{\hbar}(E_{JKM}-E_{J'K'M'})} I^{g}_{\sigma\sigma'} \tag{3.114}$$

with

$$I^{g}_{\sigma\sigma'} = 4\pi\sum_{\ell k\ell' k'} i^{\ell'}(-i)^{\ell} Q^{g\sigma\sigma'}_{\ell' k'\ell k}\sqrt{(2\ell'+1)(2\ell+1)}\, R_{k'k} S^{g}_{k'k} , \tag{3.115}$$

$$Q^{1\sigma\sigma'}_{\ell' k'\ell k} = j_{\ell'}(\kappa b_{\sigma}) j_{\ell}(\kappa b_{\sigma'}) Y_{\ell'}^{k'*}(\hat{\underline{b}}'_{\sigma}) Y_{\ell}^{k}(\hat{\underline{b}}''_{\sigma'}) = Q^{2\sigma\sigma'*}_{\ell k\ell' k'} ,$$
$$Q^{3\sigma\sigma'}_{\ell' k'\ell k} = j_{\ell'}(\kappa b_{\sigma}) j_{\ell}(\kappa b_{\sigma'}) Y_{\ell'}^{k'*}(\hat{\underline{b}}''_{\sigma}) Y_{\ell}^{k}(\hat{\underline{b}}''_{\sigma'}) , \tag{3.116}$$
$$Q^{4\sigma\sigma'}_{\ell' k'\ell k} = j_{\ell'}(\kappa b_{\sigma}) j_{\ell}(\kappa b_{\sigma'}) Y_{\ell'}^{k'*}(\hat{\underline{b}}'_{\sigma}) Y_{\ell}^{k}(\hat{\underline{b}}'_{\sigma'}) ,$$

and where

$$
\begin{aligned}
R_{k'k} &= \langle JKM|\, D^{\ell'}_{0,k'} |J'K'M'\rangle\langle J'K'M'|\, D^{\ell *}_{0,k}\, |JKM\rangle, \\
S^{1}_{k'k} &= \langle \delta n \,|\, e^{ik'\rho\alpha(t)}\, e^{-ik(1-\rho)\alpha}\, |\delta n\rangle, \\
S^{2}_{k'k} &= \langle \delta n \,|\, e^{-ik'(1-\rho)\alpha(t)}\, e^{ik\rho\alpha}\, |\delta n\rangle, \\
S^{3}_{k'k} &= \langle \delta n \,|\, e^{-ik'(1-\rho)\alpha(t)}\, e^{ik(1-\rho)\alpha}\, |\delta n\rangle, \\
S^{4}_{k'k} &= \langle \delta n \,|\, e^{ik'\rho\alpha(t)}\, e^{-ik\rho\alpha}\, |\delta n\rangle,
\end{aligned}
\tag{3.117}
$$

with ρ given by (3.50). We note that $R_{k'k}$ is given by (3.32) and its orientational average, using (3.33) becomes

$$
\langle R_{k'k}\rangle_{\Omega} = \delta_{\ell\ell'}\delta_{kk'}\delta_{k,K'-K}\,\frac{(2J'+1)}{(2\ell+1)}\begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^{2}, \tag{3.118}
$$

which implies

$$
\begin{aligned}
S^{1}_{K'-K,K'-K} &= \langle \delta n|\, e^{i(K'-K)\rho\alpha(t)}\, e^{-i(K'-K)(1-\rho)\alpha}\, |\delta n\rangle, \\
S^{2}_{K'-K,K'-K} &= \langle \delta n|\, e^{-i(K'-K)(1-\rho)\alpha(t)}\, e^{i(K'-K)\rho\alpha}\, |\delta n\rangle, \\
S^{3}_{K'-K,K'-K} &= \langle \delta n|\, e^{-i(K'-K)(1-\rho)\alpha(t)}\, e^{i(K'-K)(1-\rho)\alpha}\, |\delta n\rangle, \\
S^{4}_{K'-K,K'-K} &= \langle \delta n|\, e^{i(K'-K)\rho\alpha(t)}\, e^{-i(K'-K)\rho\alpha}\, |\delta n\rangle,
\end{aligned}
\tag{3.119}
$$

When K' = K, $S^{g} = 1$. The rotational thermal average then becomes

$$
\begin{aligned}
\langle \chi^{rot}_{\sigma\sigma'}\rangle_{T} = \frac{\pi}{Z_R}\sum_{J,K} e^{-\beta E_{JK}} \sum_{J',K'} (2J'+1)\, e^{i\frac{t}{\hbar}(E_{JK}-E_{J'K'})} \\
(x)\sum_{\ell g} Q^{g\sigma\sigma'}_{\ell,K'-K;\ell,K'-K}\begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^{2}\langle \chi^{g}_{K'-K}\rangle_{T},
\end{aligned}
\tag{3.120}
$$

where the over-all rotational partition function and torsional oscillator thermal average are

$$Z_R = \sum_{JKM} e^{-\beta\left[AJ(J+1)+(C-A)K^2\right]},$$

and

$$\langle \chi^g_{K'-K} \rangle_T = \sum_{n\delta} P_{n\delta}\, S^g_{K'-K,\,K'-K}\,, \qquad (3.121)$$

with

$$P_{n\delta} = \frac{e^{-n\beta\hbar\omega_T}}{\sum_n 3e^{-n\beta\hbar\omega_T}} = \tfrac{1}{3}\left(e^{-n\beta\hbar\omega_T}\right)\left(1-e^{-\beta\hbar\omega_T}\right). \qquad (3.122)$$

Using the Baker-Hausdorff theorem[90]

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]+\frac{1}{12}[A-B,[A,B]]+\cdots}, \qquad (3.123)$$

the torsional thermal average reduces, for g= 1, to the following

$$\begin{aligned}\langle \chi^1_{K'-K} \rangle_T &= \left\langle e^{i(K'-K)\rho\alpha(t)}\, e^{-i(K'-K)(1-\rho)\alpha} \right\rangle_T, \\ &= \left\langle e^{i(K'-K)\left[\rho\alpha(t)-(1-\rho)\alpha\right]}\, e^{\frac{1}{2}(K'-K)^2\rho(1-\rho)[\alpha(t),\alpha]} \right\rangle_T. \end{aligned} \qquad (3.124)$$

We have used the fact that $\alpha(t)$ and α commute with their commutator, which is a number.

Now invoking a corollary of Bloch's theorem[91] on the distribution function of an oscillator coordinate

$$\langle e^Q \rangle_T = e^{\frac{1}{2}\langle Q^2 \rangle_T}, \qquad (3.125)$$

where Q is any linear combination of commuting oscillator coordinates, and noting that expectation values of $\alpha^2(t)$ are the same as those of α, we find

$$\langle \chi^{1}_{K'-K} \rangle_T = e^{-\frac{1}{2}(K'-K)^2 \left[\rho^2 + (1-\rho)^2\right] \langle \alpha^2 \rangle_T + (K'-K)^2 \rho(1-\rho) \langle \alpha(t)\alpha \rangle_T}, \tag{3.126}$$

which includes the terms from the second factor of (3.124). Now it is convenient to introduce the operators a and a^+ which are conventionally employed in the quantization of the harmonic oscillator and whose commutation relations are $[a,a^+] = 1$, $[a,a] = [a^+,a^+] = 0$. Using the commutation relations, we find

$$\langle \alpha(t)\alpha \rangle_T = \frac{\hbar}{2rI_a\omega_T} \left\{ \langle aa^+ \rangle_T e^{-i\omega_T t} + \langle a^+a \rangle_T e^{i\omega_T t} \right\}, \tag{3.127}$$

where we have expanded

$$\alpha(t) = \sqrt{\frac{\hbar}{2rI_a\omega_T}} \left(a e^{-i\omega_T t} + a^+ e^{i\omega_T t} \right), \tag{3.128}$$

and where r is given by (3.45). Then,

$$\langle \alpha(t)\alpha \rangle_T = \frac{\hbar}{2rI_a\omega_T} \left\{ (\langle n \rangle_T + 1) e^{-i\omega_T t} + \langle n \rangle_T e^{i\omega_T t} \right\}, \tag{3.129}$$

where the thermal average of n is

$$\langle n \rangle_T = \sum_{nS} n P_{nS} = \frac{1}{3} e^{-\beta\hbar\omega_T}(1 - e^{-\beta\hbar\omega_T})^{-1} = \frac{1}{3}(e^{\beta\hbar\omega_T} - 1)^{-1}, \tag{3.130}$$

and similarly,

$$\langle \alpha^2 \rangle_T = \frac{\hbar}{2rI_a\omega_T} f_1(T), \tag{3.131}$$

where

$$f_1(T) = \frac{1}{3}(3e^{\beta\hbar\omega_T} - 1)(e^{\beta\hbar\omega_T} - 1)^{-1}. \tag{3.132}$$

Introducing the notation

$$
\begin{aligned}
&R_1^1(\rho)=\rho^2+(1-\rho)^2, && R_2^1(\rho)=\rho(1-\rho),\\
&R_1^2(\rho)=R_1^1(\rho), && R_2^2(\rho)=R_2^1(\rho),\\
&R_1^3(\rho)=2(1-\rho)^2, && R_2^3(\rho)=(1-\rho)^2,\\
&R_1^4(\rho)=2\rho^2, && R_2^4(\rho)=\rho^2,\\
&f_2(T)=\frac{(3e^{\beta\hbar\omega_T}-2)^{1/2}}{3(e^{\beta\hbar\omega_T}-1)},\quad G=\frac{F}{\hbar\omega_T},\quad y=e^{\beta\hbar\omega_T},
\end{aligned}
\tag{3.133}
$$

with ρ given by (3.50), the torsional oscillation thermal average is given by

$$
\langle \chi^{q}_{K'-K}\rangle_T = e^{-\frac{1}{2}GR_1^q(\rho)f_1(T)(K'-K)^2}
\otimes e^{G(K'-K)^2R_2^q(\rho)f_2(T)\left[(3y-2)^{1/2}e^{-i\omega_T t}+(3y-2)^{-\frac{1}{2}}e^{i\omega_T t}\right]}
\tag{3.134}
$$

.

Noting that the second exponential already has the form of the generating function for the modified Bessel function of the first kind,[92]

$$
e^{\frac{1}{2}x(s+\frac{1}{s})}=\sum_{n=-\infty}^{+\infty}s^n I_n(x),
\tag{3.135}
$$

we find

$$
\langle \chi^{q}_{K'-K}\rangle_T =
e^{-\frac{1}{2}GR_1^qf_1(K'-K)^2}\sum_{n=-\infty}^{+\infty}e^{-in\omega_T t}(3e^{\beta\hbar\omega_T}-2)^{n/2}I_n\left(2GR_2^qf_2(K'-K)^2\right).
\tag{3.136}
$$

The torsional oscillator thermal average above is of the same form as for a system of vibrational oscillators[11] except the explicit momentum transfer dependence in the vibrational case is replaced by a dependence on $(K'-K)^2$, factors involving ρ appear, and the mass of the vibrational oscillator is replaced by the "reduced" moment of inertia of the top about its axis of rotation. The threefold rotational degeneracy and tunneling effect has modified the form of the temperature dependence from the vibrational case. The dependence of the torsional oscillator on $(K'-K)^2$, which is the square of the difference of the quantum numbers expressing the initial and final total angular momentum projection on the internal rotation z axis, indicates that the neutron can sample only those torsional oscillator transitions which are accompanied by over-all rotational transitions about the axis of internal rotation. In this sense, we have derived a type of weak rotational selection rule which implies that the neutron "sees" the torsional motion as very strongly coupled to the over-all rotation about this axis. This feature is a result of the semi-rigid molecule assumption, but in the absence of excitation of a vibrational mode is believed to be a valid and sufficiently realistic result.

To evaluate the scattering from different molecules, we note that the translational "outer" thermal average depends on the correlation of positions of two molecules. In a gas where positions are random, the translational factor is very small (or zero), and hence outer scattering is negligible.

We are now in a position to display the double differential cross section as

$$\frac{d^2\sigma}{d\Omega dE_f} = \sum_{\sigma\sigma' g} \frac{k_f}{k_i} \frac{a_{\sigma\sigma'}}{2\pi\hbar} \int dt\, e^{-i\epsilon\frac{t}{\hbar}} e^{-\left(i\frac{t}{\hbar}+\frac{t^2}{\hbar^2\beta}\right)E_R} e^{-\kappa^2\gamma_{\sigma\sigma'}} \left\langle \chi_{\sigma\sigma'}^{n,t} \right\rangle_T \quad (3.137)$$

$$\langle \chi^{rot}_{\sigma\sigma'} \rangle_T = \frac{\pi}{Z_R} \sum_{J,K} e^{-\beta E_{JK}} \sum_{J',K'} (2J'+1) e^{i\frac{t}{\hbar}(E_{JK} - E_{J'K'})}$$

$$(\times) \sum_{\ell} Q^{g\sigma\sigma'}_{\ell,K'-K;\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2 e^{-D_g(K'-K)^2} \sum_{n=-\infty}^{+\infty} e^{-in\omega_T t} I_n\left(P_g(K'-K)^2\right)\left(3e^{\beta\hbar\omega_T}-2\right)^{n/2}. \quad (3.138)$$

Carrying out the time integral explicitly, the cross section becomes

$$\frac{d^2\sigma}{d\Omega dE_f} = \sum_{\sigma\sigma'g} a_{\sigma\sigma'} \sqrt{\frac{\pi E_f}{E_i E_R k_B T}} \; \frac{e^{-\kappa^2\gamma_{\sigma\sigma'}}}{Z_R} \sum_{J,K} e^{-\beta E_{JK}} \sum_{J'K'} (2J'+1)$$

$$(\times) \sum_{\ell} Q^{g\sigma\sigma'}_{\ell,K'-K;\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2 e^{-D_g(K'-K)^2} \quad (3.139)$$

$$(\times) \sum_{n} \left(3e^{\beta\hbar\omega_T}-2\right)^{n/2} I_n\left(P_g(K'-K)^2\right) e^{-\frac{\left[\epsilon + E_R + n\hbar\omega_T + E_{J'K'} - E_{JK}\right]^2}{4E_R k_B T}},$$

where

$$D_g = \frac{1}{2} G R_1^g(\rho) f_1(\tau), \qquad P_g = 2 G R_2^g(\rho) f_2(\tau), \quad (3.140)$$

$$\beta = 1/k_B T, \quad E_R = \frac{m}{M}\left[E_f + E_i - 2\cos\theta_s \sqrt{E_i E_f}\right]. \quad (3.141)$$

We see that the spectrum is predicted to be a sum of skewed gaussian factors each of which is appropriately weighted by the transition probability for that transition. The presence of 3-j symbols depending on five parameters with large ranges again implies that computations with (3.139) are extremely time consuming even with a digital computer, although because only the squares of 3-j symbols, which are rational fractions, appear, an approximate form for them may yet be devised. The rigid rotator cross section for symmetric molecules can be obtained from (3.139) by taking the limit as $\omega_T \to \infty$.

If we had assumed that the internal rotation in the bound case was a three-dimensional vibrational motion and treated it as an harmonic oscillator, the cross section would differ from (3.139) by replacing the factors

$$e^{-D_g(K'-K)^2}\sum_{n=-\infty}^{+\infty}\left(3e^{\beta\hbar\omega_T}-2\right)^{n/2} I_n\left(P_g(K'-K)^2\right),$$

with

$$e^{-D\kappa^2}\sum_{n=-\infty}^{+\infty} e^{n\frac{\beta}{2}\hbar\omega_T} I_n\left(P\kappa^2\right),$$

where

$$D=\frac{\hbar}{2M\omega_T}\coth\frac{\hbar\omega_T}{2k_BT},$$
$$P=\frac{\hbar}{2M\omega_T}\operatorname{csch}\frac{\hbar\omega_T}{2k_BT}. \tag{3.142}$$

This vibrational oscillator model[95] neglects the selection rule coupling internal rotational transitions to over-all rotational transitions about the axis of internal rotation and the tunneling effect through the periodic barrier. The dependence on momentum transfer is different from that of the internal rotation torsional oscillator cross section derived above, and the rotational parameters of the latter description are replaced by a vibrational mass. Since the vibrational oscillator model has no free internal rotation limit it is clearly only an approximate description. In either case, the doubly infinite sum on n is merely formal since the numerator of the skewed gaussian exponential acts as a statement of energy conservation and not all values of n are energetically possible.

We turn now to a discussion of the quantum treatment of free internal rotations in the presence of free over-all rotations. For symmetric molecules all the types of matrix elements in the free internal rotation case are of the form

$$\begin{aligned}\langle\sigma\sigma';mJKM\rangle &= \langle mJKM|e^{i\frac{t}{\hbar}H_R}e^{i\underline{\kappa}\cdot\underline{b}_\sigma}e^{-i\frac{t}{\hbar}H_R}e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}}|mJKM\rangle, \\ &= \sum_{gm'J'K'M'} e^{i\frac{t}{\hbar}(E_{mJKM}-E_{m'J'K'M'})}\Phi^{g}_{\sigma\sigma'},\end{aligned} \tag{3.143}$$

with

$$\Phi^{g}_{\sigma\sigma'} = 4\pi\sum_{\ell k\ell' k'} i^{\ell'}(-i)^{\ell}Q^{g\sigma\sigma'}_{\ell' k'\ell k}\sqrt{(2\ell'+1)(2\ell+1)}\;R_{k'k}T^{g}_{k'k}, \tag{3.144}$$

$$\begin{aligned}T^{1}_{k'k} &= \frac{1}{2\pi}\int_0^{2\pi}d\alpha\, e^{-i\alpha[(m-m')+\rho(K'-K-k')]}\int_0^{2\pi}d\alpha\, e^{-i\alpha[(m'-m-k)+\rho(K-K'+k)]}, \\ T^{2}_{k'k} &= \frac{1}{2\pi}\int_0^{2\pi}d\alpha\, e^{-i\alpha[(m-m'+k')+\rho(K'-K-k')]}\int d\alpha\, e^{-i\alpha[(m'-m)+\rho(K-K'+k)]}, \\ T^{3}_{k'k} &= \frac{1}{2\pi}\int_0^{2\pi}d\alpha\, e^{-i\alpha[(m-m'+k')+\rho(K'-K-k')]}\int d\alpha\, e^{-i\alpha[(m'-m-k)+\rho(K-K'+k)]}, \\ T^{4}_{k'k} &= \frac{1}{2\pi}\int d\alpha\, e^{-i\alpha[(m-m')+\rho(K'-K-k)]}\int d\alpha\, e^{-i\alpha[(m'-m)+\rho(K-K'+k)]}.\end{aligned} \tag{3.145}$$

Using (3.118) for $<R_{k'k}>_{\Omega}$, we find we can write

$$\begin{aligned}T^{1}_{k'k} &= \delta_{m,m'}\,\delta_{k,0} = T^{2}_{k'k}, \\ T^{3}_{k'k} &= \delta_{m+K'-K,m'}, \\ T^{4}_{k'k} &= \delta_{m,m'},\end{aligned} \tag{3.146}$$

The thermal average then becomes

$$\langle \chi^{rot}_{\sigma\sigma'} \rangle_T = \frac{\pi}{Z_{FR}} \sum_{mJK} e^{-\beta E_{mJK}} \sum_{m'J'K'} (2J'+1) e^{i\frac{t}{\hbar}(E_{mJK}-E_{m'J'K'})} \tag{3.147}$$
$$\times \sum_{\ell g} Q^{g\sigma\sigma'}_{\ell,K'-K;\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2 T^{g}_{K'-K,K'-K} ,$$

where

$$Z_{FR} = \sum_{mJKM} e^{-\beta E_{mJK}} . \tag{3.148}$$

The double differential cross section for this free internal rotation case becomes

$$\frac{d^2\sigma}{d\Omega dE_f} = \sum_{\sigma\sigma' g} a_{\sigma\sigma'} \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \int dt\, e^{-i\epsilon\frac{t}{\hbar}} e^{-(i\frac{t}{\hbar}+\frac{t^2}{\hbar^2\beta})E_R} \tag{3.149}$$
$$\times\, e^{-\kappa^2\gamma_{\sigma\sigma'}} \langle \chi^{rot}_{\sigma\sigma'} \rangle_T ,$$

which reduces to

$$\frac{d^2\sigma}{d\Omega dE_f} = \sum_{\sigma\sigma' g} a_{\sigma\sigma'} \sqrt{\frac{\pi E_f}{E_i E_R k_B T}}\, \frac{e^{-\kappa^2\gamma_{\sigma\sigma'}}}{Z_{FR}} \sum_{mJK} e^{-\beta E_{mJK}} \sum_{m'J'K'} (2J'+1) \tag{3.150}$$
$$\times \sum_{\ell} Q^{g\sigma\sigma'}_{\ell,K'-K;\ell,K'-K} \begin{pmatrix} J & J' & \ell \\ K & -K' & K'-K \end{pmatrix}^2 T^{g}_{K'-K,K'-K}\, e^{-\frac{[\epsilon+E_R+E_{m'J'K'}-E_{mJK}]}{4E_R k_B T}} .$$

This result, due to the form of $T^{g}_{K'-K,K'-K}$ and the smallness of the energy difference $E_{m'J'K'}-E_{mJK}$, is not expected to produce additional resolvable inelastic peaks to drastically change the general form of the skewed gaussian, but rather is expected to modify its shape from that expected if the molecule were rigid. The presence of general 3-j symbols is again noted, making calculations extremely lengthly.

We have presented a rigorous quantum derivation of the symmetric molecule cross section for both the bound and the free case of internal rotation, so that with sufficient effort the spectrum of scattered neutrons can be computed. We now proceed to attempt approximations which will reduce the computational burden in obtaining the cross sections to a practical level for most applications.

3.5.2 Quasi-Classical Approximations

In view of the computational problem in the quantum treatment arising from the over-all rotations, the present section is devoted to the development of a convenient approximation method for finding the cross sections and energy distributions of neutrons scattered by freely rotating symmetric molecules which possess an internal rotational degree of freedom. Krieger and Nelkin[26] have given a simple quasi-classical description of neutron scattering where the combined effects of rotation and translation of a rigid molecule are treated in terms of the Sachs-Teller "mass tensor" concept. We here attempt to generalize this method to apply to symmetric molecules with either a bound or a free internal rotational degree of freedom.

In the quasi-classical approximation, the thermal average is written as a product,

$$\langle \chi_{\sigma\sigma'} \rangle_T = \langle \chi^{t}_{\sigma\sigma'} \rangle_T \langle \chi^{r}_{\sigma\sigma'} \rangle_T \langle \chi^{v}_{\sigma\sigma'} \rangle_T, \qquad (3.151)$$

with a factor for translation, rotation, and vibration, and where we take for the vibrational factor [see Equation (3.92)].

$$\langle \chi^{v}_{\sigma\sigma'} \rangle_T = \prod_{\lambda} e^{-\frac{\hbar}{4M_\lambda \omega_\lambda}\left[(\underline{K}\cdot\underline{c}^{\lambda}_{\sigma})^2 + (\underline{K}_0\cdot\underline{c}^{\lambda}_{\sigma'})^2\right]} , \qquad (3.152)$$

so that only ground vibrational states are considered. We take for the translational factor, as before,

$$\langle \chi^{t}_{\sigma\sigma'} \rangle_T = e^{-\left(i\frac{t}{\hbar} + \frac{t^2}{\hbar^2\beta}\right)E_R} . \qquad (3.153)$$

Now consider the rotational factor for a symmetric molecule,

$$\begin{aligned}
\langle \chi^{r}_{\sigma\sigma'} \rangle_T &= \langle \psi^r | e^{i\underline{K}_0\cdot\underline{b}_\sigma(t)}\, e^{-i\underline{K}_0\cdot\underline{b}_{\sigma'}} | \psi^r \rangle_T , \\
&= \langle \psi^r | e^{i\frac{t}{\hbar}(H_{SR}+H_T)}\, e^{i\underline{K}_0\cdot\underline{b}_\sigma}\, e^{-i\frac{t}{\hbar}(H_{SR}+H_T)}\, e^{-i\underline{K}_0\cdot\underline{b}_{\sigma'}} | \psi^r \rangle_T , \qquad (3.154) \\
&= \langle \psi^r | e^{i\frac{t}{\hbar}(H_{SR}+H_T)}\, e^{-i\frac{t}{\hbar}H^{\sigma}_{SR}}\, e^{i\underline{K}_0\cdot\underline{b}_\sigma}\, e^{-i\frac{t}{\hbar}H_T}\, e^{-i\underline{K}_0\cdot\underline{b}'_{\sigma}} | \psi^r \rangle_T ,
\end{aligned}$$

where the last step defines the operator H^{σ}_{SR} , that is,

$$H^{\sigma}_{SR} = e^{i\underline{K}_0\cdot\underline{b}_\sigma}\, H_{SR}\, e^{-i\underline{K}_0\cdot\underline{b}_\sigma} , \qquad (3.155)$$

with

$$H_{SR} = \sum_{j=1}^{3} \frac{L^{i,2}_{j}}{2I_j} , \quad H_T = G_a L^{i2}_a + V(\alpha) , \quad G_a = \frac{1}{2rI_a} . \qquad (3.156)$$

Recalling the discussion of Section 3.3.1 (or see Appendix H), we have

$$L^{i}_{j} = \sum_{k} R_{jk}(q_i) L_k , \qquad (3.157)$$

where L_k is expressed in the space-fixed coordinate system, and $R(q_i)$ is the rotation operator which rotates the space-fixed system to the internal rotation coordinate system, expressed in terms of the variables $q_1 = \theta_1 = 4$, $q_2 = \cos\theta_2 = \cos\theta$, $q_3 = \theta_3 = \varphi' = \varphi + \rho\alpha$. Then we have also

$$L_j^i = \sum_\ell L_\ell R_{\ell j}(q_i), \tag{3.158}$$

which allows us to write H_{SR} in the form

$$H_{SR} = \frac{1}{2}\sum_{k\ell} L_\ell\, {}^\sigma T_{\ell k} L_k, \tag{3.159}$$

with

$${}^\sigma T_{\ell k} = \sum_j \frac{R_{\ell j}(\theta_i) R_{jk}(\theta_i)}{I_j}. \tag{3.160}$$

From the definition of H_{SR}^σ and the operator identity,

$$e^{iC} D e^{-iC} = \sum_{n=0}^{\infty} \frac{i^n}{n!}[C, D]_n \tag{3.161}$$

where $[\,,]_n$ is the nth order commutator, we find

$$H_{SR}^\sigma = \frac{1}{2}\sum_{\ell k j s}(L_\ell - B_{\ell j}^\sigma K_j)\, {}^\sigma T_{\ell k}(L_k - B_{ks}^\sigma K_s), \tag{3.162}$$

with B^σ given by

$$B_{j\ell}^\sigma = i\sum_k b_k^{\sigma\prime}[L_j, R_{k\ell}(\theta_i)], \tag{3.163}$$

such that $b^{\sigma'}$ is measured in the frame-fixed system. We can expand the expression for H_{SR}^σ as follows:

$$H^{\sigma}_{SR} = \frac{1}{2}\sum_{\ell k} L_\ell\, {}^{\sigma}T_{\ell k} L_k - \frac{1}{2}\sum_{\ell k s} L_\ell T_{\ell k} B^{\sigma}_{ks} \kappa_s$$

$$- \frac{1}{2}\sum_{j\ell k} \kappa_j B^{\sigma T}_{j\ell}\, {}^{\sigma}T_{\ell k} L_k + \frac{1}{2}\sum_{j\ell k s} \kappa_j B^{\sigma T}_{j\ell}\, {}^{\sigma}T_{\ell k} B^{\sigma}_{ks} \kappa_s , \qquad (3.164)$$

$$= H_{SR} + H_{KN} .$$

We now have from the Baker-Hausdorff theorem,[90]

$$e^{i\frac{t}{\hbar}(H_{SR}+H_T)} e^{-i\frac{t}{\hbar} H^{\sigma}_{SR}}$$

$$= e^{i\frac{t}{\hbar}\left\{(H_{SR}+H_T - H^{\sigma}_{SR} - \frac{1}{2}\left[H_{SR}+H_T , H^{\sigma}_{SR}\right] + \cdots\right\}} . \qquad (3.165)$$

In the quasi-classical approximation, we neglect all terms involving commutators of H_{SR} and H_T with H^{σ}_{SR}, so that we can write

$$e^{i\frac{t}{\hbar}(H_{SR}+H_T)} e^{-i\frac{t}{\hbar} H^{\sigma}_{SR}} = e^{i\frac{t}{\hbar}(H_{SR} - H^{\sigma}_{SR})} e^{i\frac{t}{\hbar} H_T} \qquad (3.166)$$

Corrections may thus be pursued by including the commutator contributions neglected in (3.166). All of the over-all rotational contributions (slightly modified from the rigid rotator case) will be treated as Krieger and Nelkin treated them. But the remaining terms constitute the internal rotator contributions and they will be treated on a different level of approximation—one suited to extracting the dependence of the cross section on the neutron momentum transfer to this degree of freedom.

The matrix elements now become

$$\langle \psi^{r} | e^{i\frac{t}{\hbar}(H_{SR} - H^{\sigma}_{SR})} e^{i\frac{t}{\hbar} H_T} e^{i\underline{\kappa}\cdot\underline{b}_\sigma} e^{-i\frac{t}{\hbar} H_T} e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}} | \psi^{r} \rangle ,$$

and in the quasi-classical approximation all the over-all rotation operators in $H_{SR} - H_{SR}^{\sigma}$ are treated as classical, commuting variables and the over-all rotation wave functions are replaced by rotational wave packets[26] characterized by simultaneously well-defined values of orientation and angular momentum. Such wave packets will exist when $k_BT \gg A$, and when the neutron interaction time is small compared to the over-all rotational period, i.e., when $E_i \gg (Ak_BT)^{1/2}$ where $(Ak_BT)^{1/2}$ is an estimate of the over-all rotational level spacing near the most probable level.[26] That is, in assessing the applicability of the quasi-classical approximation for over-all rotation, we expect that it gives the best agreement for high temperatures and large momentum transfers, since quantum effects in over-all rotations have been significant in observations only when the neutron energy is very low and the scattering angle small. This region of large neutron momentum transfer and high temperatures is the region of applicability of the mass-tensor approximation.[68,69]

The concept of interaction time mentioned above can be further elucidated by noting that the conditions for observations of quantum effects in over-all rotations can be stated in terms of the momentum change of the neutron at scattering.[18] The momentum change, $\hbar \underline{\kappa}$, defines a certain distance $\frac{2\pi}{\kappa}$, over which the neutron samples the motions of the atoms of the target and the appropriate "interaction time" for observations of quantum rotational effects is that required for the neutron to move the distance $\frac{2\pi}{\kappa}$:

$$t = 2\pi/\kappa v_i \qquad (3.167)$$

where $v_i = (2E_i/m)^{1/2}$ is the incident velocity of the neutron.

Now the thermal average consists of an average over molecular orientations plus an average over a Boltzmann distribution. Noting that the vibrational thermal average also involves an average over orientations, we reserve this average over orientations for a later stage in the calculations. For the average over the Boltzmann distribution the molecule will be taken to have a fixed orientation. Then in the sense of the quasi-classical approximation the thermal average of these matrix elements becomes

$$\langle \chi^{n}_{\sigma\sigma'} \rangle_T = \langle e^{i\frac{t}{\hbar}H_{KN}} \rangle_T \langle e^{i\frac{t}{\hbar}H_T} e^{i\underline{\kappa}\cdot\underline{b}_\sigma} e^{-i\frac{t}{\hbar}H_T} e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}} \rangle_T \tag{3.168}$$

where H_{KN} is essentially the rigid rotator contribution as found by Krieger and Nelkin—the small difference in the over-all rotation being due to the change in the moments of inertia about the x and y axes during a scattering event due to the relative motion of the top. Equation (3.168) in effect, ignores the coupling between internal and over-all rotations previously found.

In the bound case, we now proceed to the torsional oscillator approximation contained in the rigorous treatment, where the internal rotational wave functions are treated as harmonic oscillator wave functions in α and the internal motion is confined to small oscillations in α. Then when both atoms are in the top, we can write

$$\begin{aligned} e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}} &= e^{-i\sum\limits_{lkm}\kappa_l b^{\sigma'\,''}_{k} R_{km}(\alpha) R_{ml}(\theta_i)} \\ &\simeq e^{-i\sum\limits_{lkm}\kappa_l b^{\sigma'\,''}_{k} R_{ml}(\theta_i) - i(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3\alpha}, \\ &= e^{-i\underline{\kappa}'\cdot\underline{b}''_{\sigma'}} e^{-i(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3\alpha}, \end{aligned} \tag{3.169}$$

and because H_T is now

$$H_T = -F\frac{\partial^2}{\partial\alpha^2} + \frac{9}{4}V_3\alpha^2, \tag{3.170}$$

that is, the energy operator in α, we can also write

$$e^{i\frac{t}{\hbar}H_T} e^{i\underline{\kappa}'\cdot\underline{b}_\sigma} e^{-i\frac{t}{\hbar}H} = e^{i\underline{\kappa}'\cdot\underline{b}''_\sigma} e^{i(\underline{b}''_\sigma\times\underline{\kappa}')_3\alpha(t)}. \tag{3.171}$$

Therefore, when both atoms are in the top,

$$\begin{aligned}\langle\chi^{\gamma}_{\sigma\sigma'}\rangle_T &= \langle e^{i\frac{t}{\hbar}H_{KN}}\rangle_T \langle e^{i\underline{\kappa}'\cdot(\underline{b}''_\sigma-\underline{b}''_{\sigma'})}\rangle_T \\ &\otimes\langle e^{i(\underline{b}''_\sigma\times\underline{\kappa}')_3\alpha(t)} e^{-i(\underline{b}''_\sigma\times\underline{\kappa}')_3\alpha}\rangle_T.\end{aligned} \tag{3.172}$$

Again applying the Baker-Hausdorff theorem, the torsional thermal average becomes

$$\begin{aligned}\langle\chi^{T}_{\sigma\sigma'}\rangle_T &= \langle e^{i(\underline{b}''_\sigma\times\underline{\kappa}')_3\alpha(t)} e^{-i(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3\alpha}\rangle_T, \\ &= \langle e^{i[(\underline{b}''_\sigma\times\underline{\kappa}')_3\alpha(t)-(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3\alpha]} e^{\frac{1}{2}(\underline{b}''_\sigma\times\underline{\kappa}')_3(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3[\alpha(t),\alpha]}\rangle_T,\end{aligned} \tag{3.173}$$

which with the corollary to Bloch's theorem[91] and the fact that expectation values of $\alpha^2(t)$ are the same as those of α^2 enables us to write

$$\langle\chi^{T}_{\sigma\sigma'}\rangle_T = e^{-A_1\langle\alpha^2\rangle_T + A_2\langle\alpha(t)\alpha\rangle_T}, \tag{3.174}$$

where

$$\begin{aligned}A_1 &= \frac{1}{2}(\underline{b}''_\sigma\times\underline{\kappa}')_3^2 + \frac{1}{2}(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3^2, \\ A_2 &= (\underline{b}''_\sigma\times\underline{\kappa}')_3(\underline{b}''_{\sigma'}\times\underline{\kappa}')_3.\end{aligned} \tag{3.175}$$

By introducing the expansions

$$\alpha = \sqrt{G}\,(a + a^{+})$$
$$\alpha(t) = \sqrt{G}\,(a\,e^{-i\omega_T t} + a^{+}e^{i\omega_T t}) \tag{3.176}$$

with

$$G = F/\hbar\omega_T, \tag{3.177}$$

we found previously that

$$\langle \alpha^2 \rangle_T = G f_1(T),$$
$$\langle \alpha(t)\alpha \rangle_T = G f_2(T)\left\{(3e^{\beta\hbar\omega_T}-2)^{1/2}e^{-i\omega_T t} + (3e^{\beta\hbar\omega_T}-2)^{-1/2}e^{i\omega_T t}\right\}. \tag{3.178}$$

Hence, with the notation $y = e^{\beta\hbar\omega_T}$, the torsional thermal average is given by

$$\langle \chi^T_{\sigma\sigma'} \rangle_T = e^{-A_1 G f_1(T)}$$
$$(\times)\, e^{A_2 G f_2(T)\left\{(3y-2)^{1/2}e^{-i\omega_T t} + (3y-2)^{-1/2}e^{i\omega_T t}\right\}}. \tag{3.179}$$

The second exponential again has the form of the generating function of the modified Bessel function of the first kind, so that

$$\langle \chi^T_{\sigma\sigma'} \rangle_T = e^{-A_1 G f_1(T)} \sum_{n=-\infty}^{+\infty} e^{-in\omega_T t}(3e^{\beta\hbar\omega_T}-2)^{n/2} I_n(\chi), \tag{3.180}$$

where

$$\chi = 2A_2 G f_2(T). \tag{3.181}$$

The torsional thermal average for one atom in the top and one in the frame is simply

$$\langle \chi^{T}_{\sigma\sigma'} \rangle_{T} = e^{-A_1 G f_1(T)}, \tag{3.182}$$

and is unity when both atoms are in the frame.

To perform the averaging over molecular orientations, we note that $\langle x_{\sigma\sigma'} \rangle_T$ appears as a product of factors. Following Krieger and Nelkin, we now make the approximation that the average of the product of these factors is equal to the product of their averages. In this way we guarantee the quasi-classical rigid rotator limit.

The static interference factor is easily averaged, as follows

$$\begin{aligned} \langle e^{i\underline{\kappa}'\cdot(\underline{b}''_{\sigma}-\underline{b}''_{\sigma'})} \rangle_{\Omega} &= \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} e^{i\kappa b''_{\sigma\sigma'}\cos\theta} \sin\theta \, d\theta \\ &= j_0(\kappa b''_{\sigma\sigma'}), \end{aligned} \tag{3.183}$$

with $b_{\sigma\sigma'} = |\underline{b}_{\sigma} - \underline{b}_{\sigma'}|$, and $j_0(x) = x^{-1} \sin x$. We take the Krieger-Nelkin method of averaging in the exponent for the other factors. We have for the combined translational, over-all rotational factor

$$\langle e^{i\frac{t}{\hbar}H_{KN}} \rangle_{\Omega} = e^{-\left(i\frac{t}{\hbar}+\frac{t^2}{\hbar^2\beta}\right)E_R^{\sigma}}, \tag{3.184}$$

with

$$\begin{aligned} E_R^{\sigma} &= \hbar^2\kappa^2/2M_{eff}^{KN}, \\ M_{eff}^{KN} &= 1\Big/\tfrac{1}{3}\mathrm{Tr}\left[(M_0^{-1})_{\sigma}\right], \end{aligned} \tag{3.185}$$

where M_o^σ is the Sachs-Teller mass tensor and the average comes from taking 1/3 of the trace. For the vibrational factor, we have as before

$$\langle \chi^{v}_{\sigma\sigma'} \rangle_{\Omega} = e^{-\kappa^2 \gamma_{\sigma\sigma'}}, \tag{3.186}$$

where

$$\gamma_{\sigma\sigma'} = \frac{1}{3} \sum_{\lambda} \frac{\hbar}{4M_\lambda \omega_\lambda} \left[(C_\sigma^\lambda)^2 + (C_{\sigma'}^\lambda)^2 \right]. \tag{3.187}$$

For the torsional factor we find the orientational average of $(\underline{b}''_\sigma \times \underline{\kappa}')_3^2$ is given by

$$\langle (\underline{b}''_\sigma \times \underline{\kappa}')_3^2 \rangle_{\Omega} = \frac{1}{3} b''^2_\sigma \kappa^2 \langle \sin^2\theta \rangle_{\Omega} = \frac{2}{9} b''^2_\sigma \kappa^2 \tag{3.188}$$

We can now write the double differential cross section as

$$\begin{aligned} \frac{d^2\sigma}{d\Omega\, dE_f} = \sum_{\sigma\sigma' g} \frac{k_f}{k_i} \frac{a_{\sigma\sigma'}}{2\pi\hbar} \int dt\, e^{-i\epsilon \frac{t}{\hbar}} \Big\{ & e^{-\left(i\frac{t}{\hbar} + \frac{t^2}{\beta\hbar^2}\right) E_R^\sigma} e^{-\kappa^2 \gamma_{\sigma\sigma'}} \\ & (x)\, e^{-Q_g^{\sigma\sigma'} \kappa^2} \sum_{n=-\infty}^{+\infty} \left(3e^{\beta\hbar\omega_T} - 2\right)^{n/2} I_n(C_g^{\sigma\sigma'})\, e^{-in\omega_T t},\ j_0(\kappa b_{\sigma\sigma'}) \Big\}. \end{aligned} \tag{3.189}$$

Carrying out the time integral, the cross section is

$$\begin{aligned} \frac{d^2\sigma}{d\Omega\, dE_f} = \sum_{\sigma\sigma' g} & a_{\sigma\sigma'} e^{-\kappa^2 \gamma_{\sigma\sigma'}} j_0(\kappa b_{\sigma\sigma'}) \sqrt{\frac{\pi E_f}{\mathcal{E}_\sigma^2 E_i}}\, e^{-Q_g^{\sigma\sigma'} \kappa^2} \\ & (x) \sum_{n=-\infty}^{+\infty} \left(3e^{\beta\hbar\omega_T} - 2\right)^{n/2} I_n(C_g^{\sigma\sigma'} \kappa^2)\, e^{-\frac{\left[\epsilon + E_R^\sigma + n\hbar\omega_T\right]^2}{\mathcal{E}_\sigma^2}} \end{aligned} \tag{3.190}$$

with

$$\mathcal{E}_\sigma^2 = 4E_R^\sigma k_B T,$$
$$Q_g^{\sigma\sigma'} = \begin{cases} \frac{1}{9}Gf_1(T)\left[b_\sigma^2 + b_{\sigma'}^2\right], & (g=1,2,3) \\ 0, & (g=4) \end{cases} \tag{3.191}$$
$$C_g^{\sigma\sigma'} = \begin{cases} \frac{4}{9}Gf_2(T)\, b_\sigma b_{\sigma'}, & (g=3) \\ 0, & (g=1,2,4) \end{cases}$$

This result may be contrasted with the quasi-classical approximation to the vibrational oscillator treatment of the bound internal rotation. The cross section there is simply found to be:

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \sum_{\sigma\sigma'} a_{\sigma\sigma'} e^{-\kappa^2 \gamma_{\sigma\sigma'}} j_0(\kappa b_{\sigma\sigma'}) \sqrt{\frac{\pi E_f}{\mathcal{E}_\sigma^2 E_i}}\, e^{-D\kappa^2}$$
$$(\times) \sum_{n=-\infty}^{+\infty} e^{-n\frac{\beta}{2}\hbar\omega_T} I_n(P\kappa^2)\, e^{-\frac{[\epsilon + E_R^\sigma + n\hbar\omega_T]^2}{\mathcal{E}_\sigma^2}}, \tag{3.192}$$

with D and P given by (3.142), and with

$$E_R^\sigma = \frac{m}{M^{KN}}\left[E_f + E_i - 2\cos\theta_s\sqrt{E_i E_f}\right], \tag{3.193}$$

where

$$M^{KN} = \frac{1}{\frac{1}{3}\mathrm{Tr}\,(M_0^{-1})_\sigma} \tag{3.194}$$

and where M_0^σ is the Sachs-Teller mass tensor. That is,

$$\left[(M_0^{-1})_\sigma\right]_{ii} = \frac{b_j^2}{I_k} + \frac{b_k^2}{I_j} + \frac{1}{M},$$
$$\left[(M_0^{-1})_\sigma\right]_{ij} = -\frac{b_i b_j}{I_k}. \qquad i, j, k = 1, 2, 3 \text{ and cyclic permutations} \tag{3.195}$$

In the free internal rotation case, where $V_3 = 0$ and the internal rotational wave functions are exponentials, we have to evaluate

$$\left\langle e^{i\frac{t}{\hbar}H_T} e^{i\underline{K}\cdot\underline{b}_\sigma} e^{-i\frac{t}{\hbar}H_T} e^{-i\underline{K}\cdot\underline{b}_{\sigma'}} \right\rangle_T,$$

with

$$H_T = -F\frac{\partial^2}{\partial\alpha^2} = \frac{L_a^{i\,2}}{2rI_a} = \frac{1}{2}\sum_{kl}(L_a^i)_k C^{-1}_{kl}(L_a^i)_l, \tag{3.196}$$

where

$$C^{-1} = \begin{pmatrix} \frac{1}{rI_a} & 0 & 0 \\ 0 & \frac{1}{rI_a} & 0 \\ 0 & 0 & \frac{1}{rI_a} \end{pmatrix}. \tag{3.197}$$

Now consider

$$e^{i\underline{K}\cdot\underline{b}_\sigma} e^{-i\frac{t}{\hbar}H_T} e^{-i\underline{K}\cdot\underline{b}_{\sigma'}} = e^{-i\frac{t}{\hbar}H_T^\sigma} e^{i\underline{K}\cdot\underline{b}_\sigma} e^{-i\underline{K}\cdot\underline{b}_{\sigma'}}, \tag{3.198}$$

as defining H_T^σ to be

$$H_T^\sigma = e^{i\underline{K}\cdot\underline{b}_\sigma} H_T e^{-i\underline{K}\cdot\underline{b}_\sigma}, \tag{3.199}$$

where, using the Lie expansion [Equation(3.161)],

$$\begin{aligned} H_T^\sigma = H_T &- \frac{1}{2}\sum_{lks}(L_a^i)_l C^{-1}_{lk} D^\sigma_{ks} K_s - \frac{1}{2}\sum_{jlk} K_j D^{\sigma T}_{jl} C^{-1}_{lk} (L_a^i)_k \\ &+ \frac{1}{2}\sum_{jlks} K_j D^{\sigma T}_{jl} C^{-1}_{lk} D^\sigma_{ks} K_s, \end{aligned} \tag{3.200}$$

with

$$-D^T = D = \begin{pmatrix} 0 & 0 & d_y \\ 0 & 0 & -d_x \\ -d_y & d_x & 0 \end{pmatrix} \delta_{\sigma T_\sigma}, \tag{3.201}$$

where d_x^σ, d_y^σ are the x,y components of the distance to the z axis from the σth atom in the top. The Kronecker delta is a reminder that D = 0 for atoms not in the top. This fact implies that for different substances to within the reducing factor r, the contribution to H_T^σ is the same when the top group is the same, even if the frame group is different. Thus the presence of a CH_3 group, for example, as the freely rotating top group implies that the rotational inelastic scattering will be similar in two different molecules as long as r is not too different. Thus the use of an experimental "standard of comparison" for free internal rotation of CH_3 groups, as attempted by Janik, et al.,[55] is placed on reasonable theoretical grounds, although the fair agreement obtained by using CH_3I, which possesses no internal rotation, may imply a broader interpretation is possible than this theory affords.

However, if we further assert that the quasi-classical approximation also applies to the free internal rotation operators and wave functions, and hence replace the operators by classical, commuting variables, and effect the thermal average (reserving the average over orientations) by integrating over a Boltzmann distribution of L_a^i values in analogy to Krieger and Nelkin, then the result is a modified mass tensor. This new mass tensor is related to the old M_0^{-1} by

$$(M_E^{-1})_\sigma = (M_0^{-1})_\sigma + D_\sigma^T C^{-1} D_\sigma, \tag{3.202}$$

and its effect is to reduce the effective mass compared to the Krieger-Nelkin theory. This new effective mass can be found from taking 1/3 of the trace of the tensor whose diagonal elements are given by

$$\begin{aligned}\left[(M_E^{-1})_\sigma\right]_{xx} &= \frac{b_y^2}{I_z} + \frac{b_z^2}{I} + \frac{d_y^2}{rI_a},\\ \left[(M_E^{-1})_\sigma\right]_{yy} &= \frac{b_z^2}{I} + \frac{b_x^2}{I_z} + \frac{d_x^2}{rI_a},\\ \left[(M_E^{-1})_\sigma\right]_{zz} &= \frac{b_x^2+b_y^2}{I} + \frac{d_x^2+d_y^2}{rI_a}.\end{aligned} \tag{3.203}$$

Explicitly, the cross section is

$$\begin{aligned}\frac{d^2\sigma}{d\Omega dE_f} &= \sum_{\sigma\sigma'} a_{\sigma\sigma'} e^{-\kappa^2 \gamma_{\sigma\sigma'}} j_0(\kappa b_{\sigma\sigma'})\\ &\quad (x)\sqrt{\frac{E_f}{\pi \delta_\sigma^2 E_i}}\, e^{-\frac{[\epsilon + E_R^\sigma]^2}{\delta_\sigma^2}},\end{aligned} \tag{3.204}$$

with

$$E_R^\sigma = \frac{m}{M_{eff}^\sigma}\left[E_f + E_i - 2\cos\theta_s\sqrt{E_i E_f}\right], \tag{3.205}$$

where

$$M_{eff}^\sigma = \frac{1}{\frac{1}{3}\mathrm{Tr}(M_E^{-1})_\sigma}. \tag{3.206}$$

Thus we may summarize the results of this chapter by saying that for the two limiting cases of internal rotation we have derived rigorous quantum expressions for the neutron double differential scattering cross section appropriate to symmetric molecules. Because the free over-all rotational factors require more numerical work than the scope of this investigation allowed, suitable approximations were sought to make computation feasible so that comparison with experimental results can be made to test the theory.

In the next section we will investigate the description of the total scattering cross section and then conclude this chapter with a section comparing theory and experiment.

3.6 THE TOTAL SCATTERING CROSS SECTION

Since some experimental effort has gone into attempting to learn something about rotational dynamics of molecules from total scattering cross section measurements, we will discuss in this section the total scattering cross section for a freely rotating symmetric molecule which has an internal rotational degree of freedom. We will see that, in general, it is different from that of a molecule without this degree of freedom.

We note that the quantum expressions for the double differential cross sections derived in the previous section are not easily integrated over energy and angle, and that the following gives a more general result. To evaluate the angular differential cross section, which can be written as,

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i N} \sum_{i,f} P_i \left| \langle f | \sum_{j\sigma} a_{j\sigma} e^{i \underline{\kappa} \cdot \underline{R}_{j\sigma}} | i \rangle \right|^2 , \qquad (3.207)$$

we require $\underline{b}_{j\sigma}$ expressed in Euler angles and the appropriate rotational wave functions. This is in accordance with our separate treatment of rotations and will allow us to investigate the effect of the internal rotational degree of freedom.

For convenience we again choose the z axis along $\underline{\kappa}$ so that the cross section becomes

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i N} \sum_{i,f} P_i \left| \langle f | \sum_{j\sigma} a_{j\sigma} e^{i\kappa z_{j\sigma}} | i \rangle \right|^2, \tag{3.208}$$

where $z_{j\sigma}$ is the z component of $\underline{b}_{j\sigma}$. For an atom in the frame, we find

$$z_{j\sigma} = z'_{j\sigma} \cos\theta + x'_{j\sigma} \sin\theta \sin(\varphi' - p\alpha). \tag{3.209}$$

The appropriate rotational wave functions are

$$|i\rangle = |\delta n J K M\rangle = N_{nJKM} D^{J}_{-M,-K}(\psi\theta\varphi') M_{\delta n K}(\alpha), \tag{3.210}$$

and are taken to be the general solutions of the eigenvalue problem for a rigid rotator with an internal rotational degree of freedom so that M(α) are the Mathieu functions satisfying the quasi-periodic boundary condition. However, it will now be profitable to expand M(α) in a Fourier series using Floquet's theorem as follows:

$$M_{\delta n K}(\alpha) = e^{-iKp\alpha} \sum_{k=-\infty}^{+\infty} C_k(\delta, n, K) e^{ik\alpha}, \tag{3.211}$$

where the C_k are Fourier coefficients which depend on δ, n, and K, and are tabulated.[88]

We proceed by substituting (3.209) and (3.210) into (3.208), obtaining

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i N} \sum_{\substack{\delta n J K M \\ \delta' n' J' K' M'}} P_{\delta n J K M} \left| \sum_{j\sigma} a_{j\sigma} \int e^{i\kappa [z'_{j\sigma} \cos\theta + x'_{j\sigma} \sin\theta \sin(\varphi' - p\alpha)} N_{n J' K' M'} N_{n J K M} \right. \tag{3.212}$$

$$\left. D^{J'*}_{-M',-K'}(\psi\theta\varphi') D^{J}_{-M,-K}(\psi\theta\varphi') M^{*}_{\delta' n' K'}(\alpha) M_{\delta n K}(\alpha) \sin\theta \, d\theta \, d\psi \, d\varphi' \, d\alpha \right|^2.$$

From (3.211) the product of the Mathieu functions can be expressed as

$$M^{*}_{\delta' n' K'}(\alpha)\, M_{\delta n K}(\alpha) = e^{-i(K-K')p\alpha} \sum_{k=-\infty}^{+\infty} \nu_k\, e^{ik\alpha}, \qquad (3.213)$$

where

$$\nu_k = \sum_{m=-\infty}^{+\infty} C_m(\delta, n, K)\, C_{m-k}(\delta', n', K'), \qquad (3.214)$$

and making the variable transformation

$$\varphi = \varphi' - p\alpha, \qquad (3.215)$$

the cross section becomes

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i N} \sum_{\substack{\delta n J K M \\ \delta' n' J' K' M'}} P_{\delta n J K M} \left| \sum_{j\sigma k} a_{j\sigma} \nu_k \int e^{iK\left[z'_{j\sigma}\cos\theta + x'_{j\sigma}\sin\theta\sin\varphi\right]} \right. \qquad (3.216)$$

$$\left. \times N_{n'J'K'M'} N_{nJKM} D^{J'*}_{-M',-K'}(\psi\theta\varphi) D^{J}_{-M,-K}(\psi\theta\varphi)\, e^{ik\alpha} \sin\theta\, d\theta\, d\psi\, d\varphi\, d\alpha \right|^2 .$$

The integral on α can be done as follows:

$$\frac{1}{2\pi}\int_0^{2\pi} e^{ik\alpha}\, d\alpha = \frac{\sin k\pi}{k\pi}\left[\cos k\pi + i\sin k\pi\right] = \delta_{k0}, \qquad (3.217)$$

which is nonzero only for k=0 when it equals 1. The resulting expression for the k=0 term is simply ν_0^2 times

$$\left(\frac{d\sigma}{d\Omega}\right)_{J'K'M',JKM} = \left| \sum_{j\sigma} a_{j\sigma} \int e^{iK\left[z'_{j\sigma}\cos\theta + x'_{j\sigma}\sin\theta\sin\varphi\right]} N_{J'K'M'} N_{JKM} \right. \qquad (3.218)$$

$$\left. \times D^{J'*}_{-M',-K'}(\psi\theta\varphi) D^{J}_{-M,-K}(\psi\theta\varphi) \sin\theta\, d\theta\, d\psi\, d\varphi \right|^2 ,$$

which is identifiable with the differential cross section of an atom in a free rotator undergoing a transition from $|JKM>$ to $|J'K'M'>$. However, this partial cross section must be averaged over a Boltzmann distribution appropriate to the states $|\delta_n JKM>$ and summed over all final states similarly labeled. Integration over Ω gives the total scattering cross section:

$$\sigma_T(E_i) = \frac{1}{k_i N} \sum_{\delta_n JKM} P_{\delta_n JKM} \sum_{\delta'_{n'} J'K'M'} k_f \vartheta_0^2(\delta, \delta', n, n', K, K') \otimes \sigma_T^{RR}(JKM, J'K'M'), \tag{3.219}$$

where

$$\vartheta_0 = \sum_{k=-\infty}^{+\infty} C_k(\delta, n, K)\, C_k(\delta', n', K'). \tag{3.220}$$

From the conditions

$$\sum_{k=-\infty}^{+\infty} C_k^2(\delta, n, K) = 1, \quad \sum_{k=-\infty}^{+\infty} C_k^2(\delta', n', K') = 1, \tag{3.221}$$

which follow from the normalization of the wave function, application of Cauchy's inequality leads to the result that

$$\vartheta_0 = \sum_{k=-\infty}^{+\infty} C_k(\delta, n, K)\, C_k(\delta', n', K') \leq 1. \tag{3.222}$$

This result has been found independently by Kolos.[96]

Equation (3.219) gives the cross section of an atom in the frame. In considering an atom in the top whose z-component is given by,

$$z_{j\sigma} = z''_{j\sigma} \cos\theta + x''_{j\sigma} \sin\theta \sin[\varphi - (1-\rho)\alpha], \tag{3.223}$$

we may expand the Mathieu function as follows

$$M_{\delta n K}(\alpha) = e^{iK(1-\rho)\alpha} \sum_{k=-\infty}^{+\infty} C_k(\delta, n, K)\, e^{i(k-K)\alpha}, \tag{3.224}$$

so that the product becomes

$$M^{*}_{\delta' n' K'}(\alpha)\, M_{\delta n K}(\alpha) = e^{i(K'-K)(1-\rho)\alpha} \sum_{k=-\infty}^{+\infty} \nu_k\, e^{i[k-(K-K')\alpha]}, \tag{3.225}$$

where

$$\nu_k = \sum_{m=-\infty}^{+\infty} C_m(\delta, n, K)\, C_{m-k-(K'-K)}(\delta', n', K'), \tag{3.226}$$

and substitute (3.223) and (3.225) into (3.208) to obtain (3.219) again, but now ν_0 is given by (3.226) instead of (3.220), and $\nu_0 \leq 1$ holds. Using the recursion relation,[76]

$$C_{m-l}(\delta, n, K) = C_m\left(\delta, n, K + l\frac{I_z}{I_a}\right), \tag{3.227}$$

we can rewrite (3.226) for k=0, as

$$\nu_0 = \sum_{m=-\infty}^{+\infty} C_m\left(\delta, n, -K\frac{(1-\rho)}{\rho}\right) C_m\left(\delta', n', -K'\frac{(1-\rho)}{\rho}\right). \tag{3.228}$$

At this point we can again observe the special nature of the free over-all rotations about the internal rotation axis. Unless either the internal rotational state or the free over-all rotational state about the internal rotation axis changes during scattering, ν_0^2 will equal unity, and the cross section will be the same as for a freely rotating rigid molecule. However, when either or both of the above transitions occur, the cross section will be lower than that for a freely rotating rigid molecule since ν_o^2 will be less than unity.

We now need a convenient way to obtain the partial cross section for a free rigid rotator, in order to quantitatively predict the total cross section. We also need to account for the vibrational and translational effects which have been neglected so far here. However, we can immediately understand, qualitatively, the empirical technique employed by Rush[50] and others, in which the height of the barriers to internal rotation are estimated by calibrating the slopes of total cross section measurements at very low neutron energy.

For a given value of V_3, ν_o^2 will be smaller at larger neutron energy where greater change in K occurs, thus the slope of σ_T with increasing E_i will be more negative for a molecule with an internal rotational degree of freedom than for a similar rigid molecule. But, the calibration is possible because for a given change in K, ν_o^2 is smaller for smaller internal barriers, thus leading to relatively more negative slopes for lower barriers. In this energy range, the scattering would be elastic with respect to the internal rotational transitions, which are presumed to be only ground-ground transitions.

Attempts to calculate the partial cross section and thus put this total cross section description on a quantitative basis have proved impractical due to the problem of finding and summing all the great number of contributions associated with all possible transitions. However, in the special case of free internal rotation an alternative method is available due to the form of the quasi-classical cross section given in (3.204), which can be directly integrated to give

$$\sigma_T(E_i) = \sum_{\sigma} \frac{\pi a_{\sigma\sigma} \hbar^2}{2m\gamma_{\sigma\sigma} E_i} \left\{ \operatorname{erf}\left[\left(\frac{M_{\mathrm{eff}}^{\sigma} E_i}{m k_B T}\right)^{1/2}\right] - \left(\frac{\delta}{1+\delta}\right)^{1/2} e^{-\frac{M_{\mathrm{eff}}^{\sigma} E_i}{m k_B T(1+\delta)}} \operatorname{erf}\left[\left(\frac{M_{\mathrm{eff}}^{\sigma} E_i \delta}{m k_B T(1+\delta)}\right)^{1/2}\right] \right\}, \tag{3.229}$$

where

$$\delta = \frac{\hbar^2 [(m + M_{\mathrm{eff}}^{\sigma})/m]^2}{8 M_{\mathrm{eff}}^{\sigma} \gamma_{\sigma\sigma} k_B T}, \tag{3.230}$$

and $M_{\mathrm{eff}}^{\sigma}$ is given by (3.206), remembering $D_\sigma = 0$ for σ in the frame. The function erf(x) is defined as,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \tag{3.231}$$

for which 5 or 6 place tables should be used in computing (3.229).

3.7 SLOW-NEUTRON SCATTERING BY SEVERAL SUBSTANCES

In this section we will compare calculations, using the theory developed in the previous sections, with experimental results. This is always the test of any theory or model. We present double differential scattering cross section comparisons for gaseous ethane and liquid dimethyl acetylene and a total scattering cross section comparison for liquid dimethyl acetylene. Of course, comparison with the rigorous quantum results is not made here, although this would have been highly desirable. Comparison with the quasi-classical approximation is deemed to be more a test of the approximations used than of the rigorous result from which it is derived.

Ethane, C_2H_6, is a symmetric molecule consisting of two methyl groups connected by a single carbon-carbon bond. Its structure has been summarized by Straker,[95] who recently made the differential neutron cross section measurements. Selection rules prohibit the excitation of the internal torsional motion about the c-c bond by electromagnetic radiation so that direct observation of internal torsional transitions by Raman or infrared spectroscopy is not possible, although combination bands have been measured. Direct evidence for the internal torsional mode is provided by the scattered neutron energy distributions. Figure 3 displays the experimental[95] and theoretical curves for gaseous ethane at a forward angle where the torsional oscillation transition of .034 ev is believed to be evident. Only the direct scattering was calculated. The curves have been normalized at the rotational-translational maximum, which is seen to be narrower than the theoretical prediction and somewhat displaced. This is believed to be due to quantum over-all rotational effects in the experimental data. Similar effects have been noted in neutron spectra for methane and a quasi-classical approximation calculation. A calculation with a quantum treatment of rotations gave both a narrower and slightly displaced peak in better agreement with experiment.[67] This would seem to underline the desirability of calculating the quantum result for ethane including the internal rotation.

Dimethyl acetylene, $CH_3-C \equiv C-CH_3$ is a symmetric molecule and is believed to be an example of free internal rotation. The molecule has no permanent dipole moment. Its structure is summarized as: symmetry of point group D'_{3h}; $r_{C\equiv C} = 1.204$ Å, $r_{c-c} = 1.464$ Å, $r_{CH} = 1.093$ Å, and $< HCH = 109°28'$.

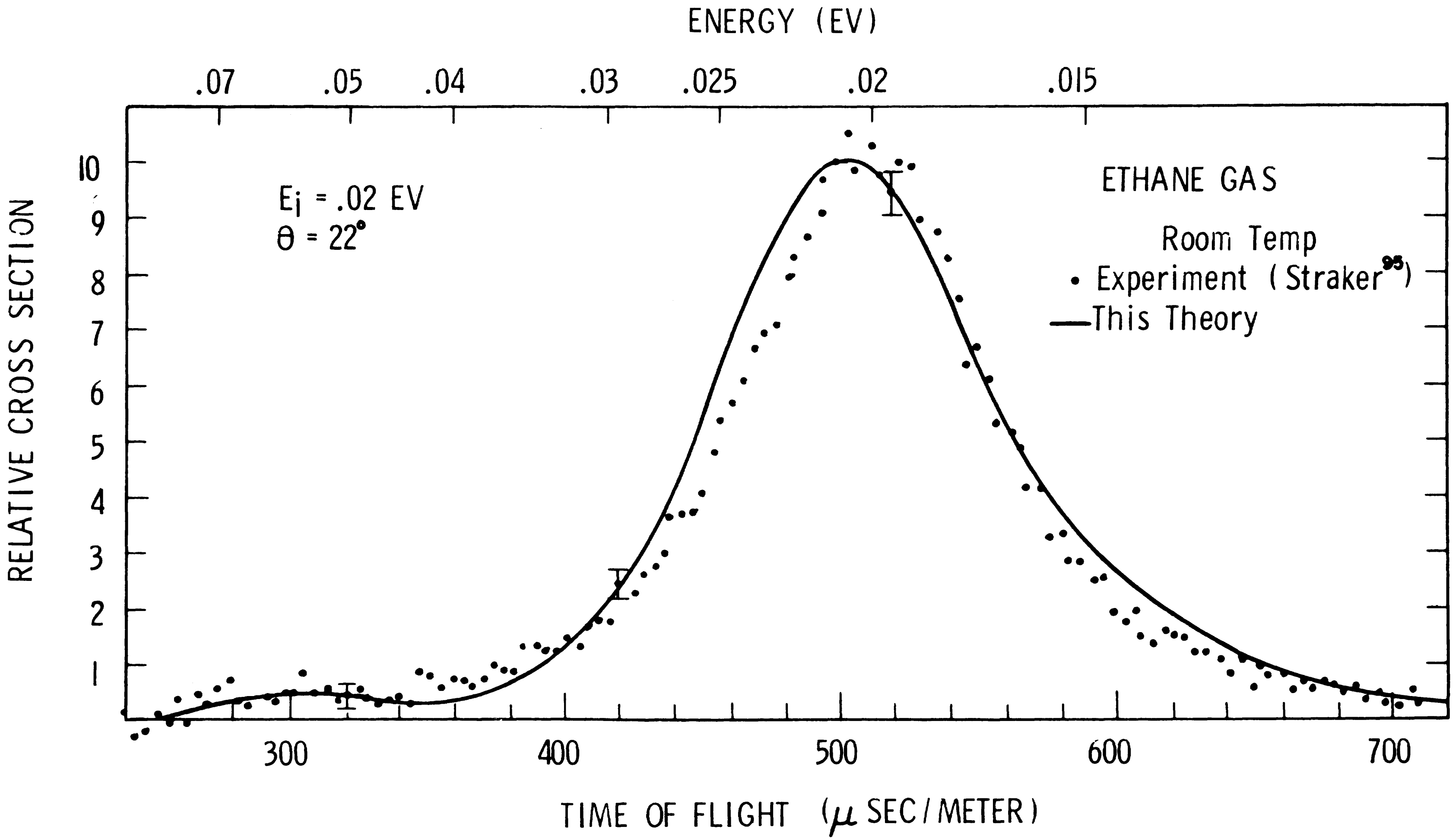


Figure 3. Relative differential scattering cross section of gaseous ethane at a scattering angle of 22°.

As in ethane, selection rules prohibit observation of the internal rotation using electromagnetic radiation. Infrared and Raman measured vibrational frequencies are summarized by Herzberg.[38] Specific heat and entropy determinations point strongly to free internal rotation, as does the neutron scattering data. Figure 4 is a comparison of the normalized differential cross sections, experimental[55] and theoretical, where the free internal rotation expression (3.204) was used. Interference scattering was again neglected in the calculations, although the data shows some disagreement in the region of the quasi-elastic scattering where interference effects would contribute.

The total scattering cross section of liquid dimethyl acetylene is shown in Figure 5 where the experimental data[51] and two theoretical curves are shown. The calculated curves were obtained from (3.229) using the effective mass of this theory, M^{σ}_{eff}, and the Krieger-Nelkin effective mass, M^{KN}.

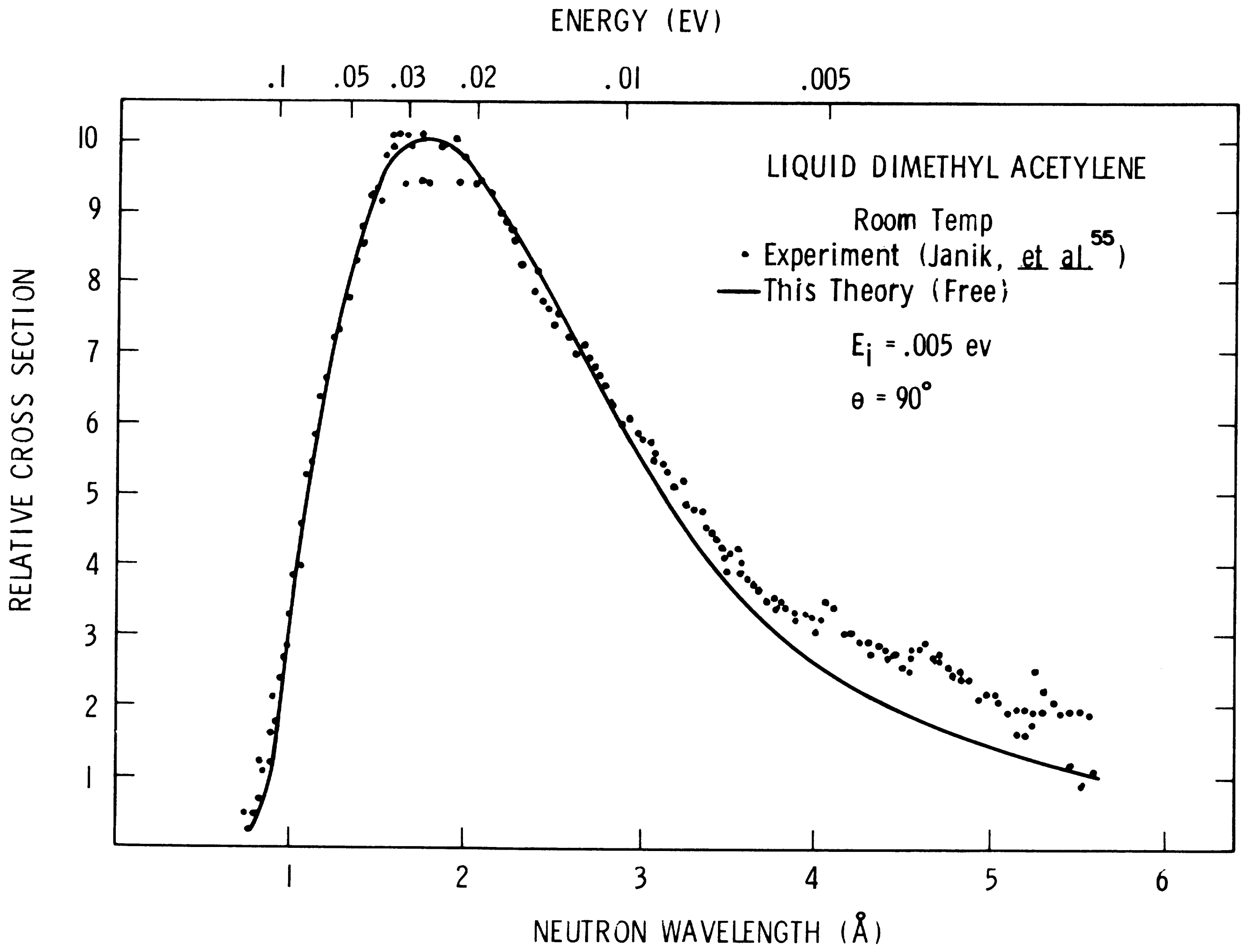


Figure 4. Relative differential scattering cross section of liquid dimethyl acetylene at a scattering angle of 90°.

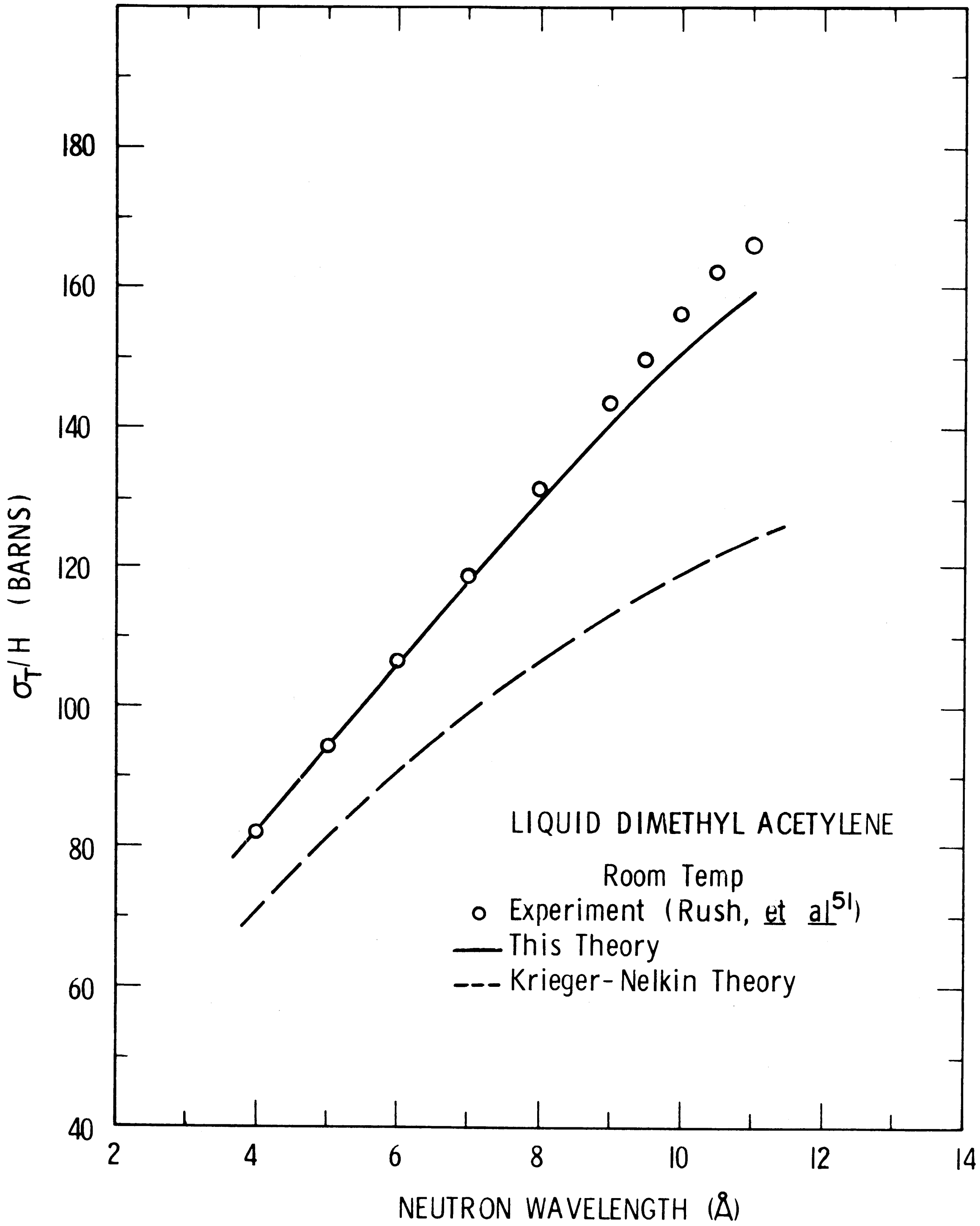


Figure 5. Total scattering cross section per hydrogen atom for liquid dimethyl acetylene.

CHAPTER IV

SLOW-NEUTRON SCATTERING AND HINDERED OVER-ALL ROTATION OF MOLECULES WITH INTERNAL ROTATION

> "It has been long understood that approximate solutions of scientific problems may be obtained by limitations of the data, such as enables us easily to solve the modified form of the question, while we are well assured that the circumstances (so modified) affect the result only in a superficial manner."
>
> Thomson and Tait (1872)

4.1 INTRODUCTION

In the previous chapter, we investigated the effect of an internal rotational degree of freedom upon the inelastic scattering of neutrons from molecules when the over-all rotations are completely free as they are in gases. The treatment is therefore not applicable to molecular systems in which appreciable orientation-dependent intermolecular forces are known to exist. For such systems a more realistic description of molecular over-all rotations involves hindered rather than free rotational motions. That is, if existing intermolecular forces in condensed systems are sufficiently strong to cause the molecules to spend considerable periods of time in certain preferred orientations of minimum energy, then whole-body rotations of the molecules will be hindered or restrained by these forces.

Various possible mechanisms might be involved which give rise to this hindrance of over-all rotation. Molecules and ions in many crystals can rotate at their lattice sites and the relative rotational freedom may be important in studying the properties of the crystals, such as the ferroelectric effect, etc. Several authors have discussed the theory of molecular and ionic rotation in solids from the quantum mechanical viewpoint[96-101]. Although this solid state problem is closely related to that of internal rotation, it is a distinctly different problem and will not be discussed further here.

The work of Debye,[102] Onsager,[103] Kirkwood,[104] and Frenkel[105] on the polarization of polar liquids involved the concept of a local electric field which represents the effect of the dipoles of the near neighbors. This idea has been employed by Yip and Osborn[106,107] to describe the hindrance of rotation of rigid polar molecules in liquids and was applied to water. They ignored the effect of hydrogen bonding in that the field replaced only the effect of the dipoles of the nearby molecules. However, within the spirit of this model it may be possible to re-interpret this electric field as also representing the orientating effect of a single, weak hydrogen bond, i.e.,

$$\underline{E}_{local} = \underline{E}_{dipole} + \underline{E}_{bond},$$

thus permitting application of the hindered rotator model to associated liquids of molecules with single "bonding."

The term "hydrogen bond" was coined by Latimer and Rodebush[108] to characterize the energy of interaction between an OH (or NH) group and O, N, F, or Cl atoms. Hydrogen bonds are usually electrostatic interactions, although the character changes from electrostatic to homopolar when the groups are squeezed together.[109]

Justification for this interpretation is provided by the fact that the dipole interaction is a long range interaction, decreasing only as the cube of the distance between two molecules whereas the van der Waals forces decrease as the seventh power of the distance, and hence the orientations of polar molecules are more strongly correlated than nonpolar molecules. Thus the inclusion of a much shorter range orientating effect may be permissible. The agreement of the theory and experiment in the case of water, which is a prime example of hydrogen bonding association, further supports this view, especially since only the approximate magnitude of the field is provided by the theory. We hold this interpretation in abeyance, however, since an experimental test is suggested by the considerations of this chapter. In any case, when the bonds are sufficiently strong to cause chains of polymers to form, the single-particle assumption would need to be reinterpreted.

In this chapter we will investigate the effect of internal rotation in the presence of hindered over-all rotation of molecules in liquids. For purposes of understanding we review the derivation of the hindered rotator wave functions as they are needed. We will see that here in contrast to the free over-all rotation case calculations of the quantum result are reasonable due to the effect of the hindering forces.

We assume that this hindrance is predominantly caused by electrostatic interactions among molecular dipoles and that the interaction of a molecular dipole with the dipoles of its nieghbors can be described in terms of the coupling of the molecular dipole moment to a local electric field which represents the net effect arising from the presence of the near neighbors. Although our prime concern here is with the liquid state the above reasoning applies equally well to the molecular crystalline state.

If these molecules further possess an internal rotational degree of freedom, it may or may not be significantly affected by the close proximity of other molecules. Various effects may change the effective barrier to internal rotation. Without a clear understanding of the origin of the internal barrier, one must consider the possibility in hydrogeneous associated liquids that hydrogen bonding between molecules may tend to change the effective barrier to internal rotation through a bonding, bond-bending, or saturation mechanism of some kind due to the "antagonism" of external and internal "bonds." Another effect may be due to having so many molecules within the "volume of influence" of a given molecule that the close proximity further hinders the rotation of the frame relative to the top and hence increases the effective internal barrier. In any case, we assume that the only effect would be to change the internal barrier height.

The presence of internal rotation does not affect the dipole moment which one ascribes to a symmetric molecule. The electric field in this approach will be taken to be temperature independent, uniform in the immediate vicinity of the molecule, and constant for an interval of time at least as long as a period of over-all rotation. Furthermore, it is presumed that these "order intervals" are long compared to neutron-nuclear interaction times. We will assume the magnitude of the local electric field in liquids near the freezing point is of the same order as the crystalline field in the corresponding solid phase. Spatial and time dependences of the electric field can be assigned physical meanings and may be introduced as modifications of the present approach.

4.2 THE ROTATIONAL HAMILTONIAN

The Hamiltonian now becomes

$$H_{HR} = H_R - \underline{\mu} \circ \underline{E}, \qquad (4.1)$$

where H_R is given in the internal rotation discussion for gases and normal liquids. The direction of the electric field is fixed for a given molecule; however, in evaluating the matrix elements for hindered over-all rotation its direction will be averaged, in which case it will be assumed to have random orientation.

If the dipole moment $\underline{\mu}$ is chosen along the frame-fixed z axis and if the electric field $\underline{E}$ is chosen along the space-z axis, then the potential $-\underline{\mu}\cdot\underline{E}$ is simply $-\lambda \cos \theta$ where $\lambda = \mu E$. In the presence of the potential the total angular momentum is not conserved, but since the three Euler angles ψ, φ', and α are not affected by $\underline{E}$, then M and K and the quantum numbers associated with α remain good quantum numbers while R is anticipated as a replacement for J.

The rigorous solution of the symmetric molecule hindered over-all rotation problem, due to the large amount of numerical work required to obtain wave functions, energies, and matrix elements, is not convenient.

However, the physically interesting strong coupling case implied by the existence of hindered over-all rotations can be more easily treated.

The eigenvalue problem for symmetric polar molecules with an internal rotational degree of freedom in an electric field is

$$(H_{HR} - E)\Lambda(\psi\theta\varphi'\alpha) = 0, \tag{4.2}$$

where now

$$\begin{aligned} H_{HR} = -A\Bigg[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\bigg\{\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi'} \\ + \left(\frac{I}{I_z}\sin^2\theta + \cos^2\theta\right)\frac{\partial^2}{\partial\varphi'^2}\bigg\}\Bigg] - F\frac{\partial^2}{\partial\alpha^2} - \lambda\cos\theta + V(\alpha). \end{aligned} \tag{4.3}$$

The eigenvalue equation is separable due to the form of the Hamiltonian, and so the wave function is of the form

$$\Lambda(\psi\theta\varphi'\alpha) = e^{iM\psi}e^{iK\varphi'}Y(\theta)M(\alpha), \tag{4.4}$$

where $Y(\theta)$ is given by

$$\begin{aligned} \Bigg[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{(M - K\cos\theta)^2}{\sin^2\theta} \\ - \frac{I}{I_z}K^2 + \frac{1}{A}(\lambda\cos\theta + E)\Bigg]Y(\theta) = 0, \end{aligned} \tag{4.5}$$

and $M(\alpha)$ is formally given by

$$\left[F\frac{d^2}{d\alpha^2} + E_n - \frac{V_3}{2}(1 - \cos 3\alpha)\right]M(\alpha) = 0, \tag{4.6}$$

with the boundary condition (3.83), but will be approximated by harmonic oscillator functions or exponentials depending upon the relative magnitude of V_3 and E_n.

Under the influence of a strong electric field the molecular dipole will tend to be aligned in the direction of the field, thus restricting angle θ to small values and hindering the rotation of the molecule as a whole. However, the molecule may still rotate about its symmetry axis and rotate internally as well. A power series expansion to second order in θ gives

$$\left[\frac{d^2}{d\theta^2}+\left(\frac{1}{\theta}-\frac{\theta}{3}\right)\frac{d}{d\theta}-\frac{(M-K)^2}{\theta^2}-\left(\frac{I}{I_z}-\frac{2}{3}\right)K^2 - \frac{M}{3}(K+M)+\frac{\lambda+E}{A}-\frac{\lambda\theta^2}{A}\right]Y(\theta)=0. \tag{4.7}$$

Using sequential variable transformations

$$\begin{aligned} Y(\theta) &= F(\theta)\, e^{\theta^2/12}, \\ x &= \eta\theta^2, \\ P(x) &= F(\theta), \end{aligned} \tag{4.8}$$

yields

$$\frac{d}{dx}\left(x\frac{dP}{dx}\right)-\frac{1}{4}\left(\frac{\delta^2}{x}+x-\frac{\beta}{\eta}\right)P(x)=0, \tag{4.9}$$

where

$$\delta=(M-K),$$
$$\beta=\frac{\lambda+E}{A}-\left(\frac{I}{I_z}-\frac{2}{3}\right)K^2-\frac{M}{3}(K+M), \qquad (4.10)$$
$$\eta=\left(\frac{\lambda}{2A}-\frac{1}{36}\right)^{1/2}.$$

The differential equation in x may be further transformed by noting that its well behaved solutions near its singular points ($x = 0,\infty$ where the range of θ is 0 to ∞ in the small angle approximation instead of 0 to π) are

$$P(x) \underset{x\to 0}{\approx} x^{|\delta|/2}$$
$$\underset{x\to\infty}{\approx} e^{-x/2},$$

thereby suggesting the transformation $P(x) = x^{|\delta|/2}e^{-x/2}L(x)$, which leads to an equation for $L(x)$:

$$x\frac{d^2L}{dx^2}+(|\delta|+1-x)\frac{dL}{dx}+\left(\frac{\beta}{4\eta}-\frac{|\delta|+1}{2}\right)L(x)=0, \quad (4.11)$$

which is in the form of the confluent hypergeometric equation with a regular singular point at $x = 0$ and an irregular point at $x = \infty$. The solution, like that of the hypergeometric equation, can be expressed as a convergent power series for $|x| < 1$, where the requirement of square integrability everywhere in turn requires that $R \equiv \beta/4\eta - (|\delta|+1)/2$ be a non-negative integer and hence the solutions are the associated Laguerre polynomials

$L_R^{|M-K|}(x)$. The above condition also determines that the over-all rotation energy eigenvalues are given to second order by

$$E_{RKM} = \sqrt{2\lambda A}\left(2R + |M-K| + 1\right) - \lambda + A\left[\left(\frac{I-I_z}{I_z}\right)K^2 + MK - \frac{1}{4}\left\{2R(R+1) - 2R|M-K| + |M-K| - |M-K|^2 + 2\right\}\right], \qquad (4.12)$$

where contributions from terms ignored in the differential equation in θ but which contribute to the energy of order A, have been included.[106] Formally the range of R is 0,1,...,∞, and of K and M is 0, ±1,..,±∞. The eigenvalues above are valid for $\lambda \gg A$ and the corresponding over-all rotational wave functions are

$$|RKM\rangle = N_{RKM}\, e^{iM\psi} e^{iK\varphi'} \chi^{\frac{|M-K|}{2}} e^{-\frac{\chi}{2}} L_R^{|M-K|}(\chi), \qquad (4.13)$$

where N_{RKM} is determined to be, from a special case of a more general integral evaluated in Appendix I:

$$N_{RKM} = \left(\frac{\eta R!}{2\pi^2\left[(R+|M-K|)!\right]^3}\right)^{1/2}. \qquad (4.14)$$

One further restriction must be placed upon this hindered over-all rotation model. Not all the solutions derived above are admissible since the expectation value of θ in a particular state can be expressed as

$$\langle\theta^2\rangle_{RKM} = \sqrt{\frac{2A}{\lambda}}\left(2R+|M-K|+1\right), \qquad (4.15)$$

and there will be values of R and $|K-M|$ for which $\langle\theta^2\rangle_{RKM}$ is no longer small.

We are now in a position to discuss the "rotational" energies of a polar symmetric molecule in the liquid state:

$$E_{nRKM} = E_{RKM} + E_n , \qquad (4.16)$$

which are seen to consist of contributions from hindered over-all rotation, free over-all rotation (the terms proportional to A), and either free internal rotation or torsional oscillation. The hindered internal rotations give rise to equally-, but widely-spaced energy levels, while the hindered over-all rotational motion gives rise to a pattern of levels generally intermediately spaced between the above levels and those of the more closely-spaced, complicated pattern of free over-all rotations, which have the same order of magnitude level spacing as what one may expect for the possible hindered translational levels in a liquid. That a superposition of all of these levels may be observed in inelastic neutron scattering simply as a "rotation" band is certainly reasonable, since the resulting line shape, even in a reasonably good resolution experiment, will likely appear as a broad distribution rather than a single sharp line. The free over-all rotational levels correspond to free rotation of the molecule about the axis of internal rotation and free rotation of the molecular z-axis about the direction of the local electric field.

4.3 MATRIX ELEMENTS OF THE NEUTRON OPERATOR

We now proceed to calculate the appropriate rotational matrix elements for neutron scattering by a polar liquid whose molecules possess an internal rotational degree of freedom.

For a single symmetric molecule the appropriate rotational matrix elements in the bound case are all of the form

$$\langle \sigma\sigma' ; \delta n R K M \rangle = \langle \delta n R K M | e^{i\underline{\kappa}\cdot\underline{b}_\sigma(t)} e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}} | \delta n R K M \rangle \tag{4.17}$$

It is advantageous to first perform the average over the electric field orientation. Dependence upon this direction is made explicit by the expansions

$$e^{i\underline{\kappa}\cdot\underline{b}_\sigma} = 4\pi \sum_{lkm\mu} i^l j_l(\kappa b_\sigma) Y_l^{k*}(\hat{\underline{b}}'_\sigma) Y_l^{\mu}(\hat{\underline{\kappa}}^\circ) D^l_{m,k}(\psi\theta\varphi') \\ (x)\, D^l_{\mu,m}(\alpha'\beta'\gamma') e^{ik\rho\alpha} ,$$

$$e^{i\underline{\kappa}\cdot\underline{b}_{\sigma'}} = 4\pi \sum_{lkm\mu} i^l j_l(\kappa b_{\sigma'}) Y_l^{k*}(\hat{\underline{b}}''_{\sigma'}) Y_l^{\mu}(\hat{\underline{\kappa}}^\circ) D^l_{m,k}(\psi\theta\varphi') \\ (x)\, D^l_{\mu,m}(\alpha'\beta'\gamma') e^{-ik(1-\rho)\alpha} , \tag{4.18}$$

where the σth atom is in the frame and the σ'th is in the top, where $\underline{\kappa}^\circ$ has components in the laboratory coordinate system, and where the orientation of the space axes (along whose z axis the field is directed) with respect to the fixed laboratory axes is specified by the Euler angles $(\alpha'\beta'\gamma')$.

To obtain an expression for the matrix elements averaged over all the random directions of $\underline{E}$, we write for g = 1,

$$\langle \sigma\sigma'; \delta n RKM \rangle'_{av} = \sum_{R'K'M'} e^{i\frac{t}{\hbar}(E_{RKM} - E_{R'K'M'})} \frac{1}{8\pi^2}$$

$$(\times) \int d\Omega(\alpha'\beta'\gamma') \langle \delta n RKM | 4\pi \sum_{\ell' k' m' \mu'} i^{\ell'} j_{\ell'}(\kappa b_\sigma) Y_{\ell'}^{k'*}(\hat{\underline{b}}_\sigma) Y_{\ell'}^{\mu'}(\underline{\kappa}^\circ)$$

$$(\times) D^{\ell'}_{m';k'} D^{\ell'}_{\mu';m'}(\alpha'\beta'\gamma') \, e^{ik'\rho\alpha(t)} | R'K'M' \rangle \qquad (4.19)$$

$$(\times) \langle R'K'M' | 4\pi \sum_{\ell k m \mu} (-i)^{\ell} j_\ell(\kappa b_{\sigma'}) Y_\ell^{k}(\hat{\underline{b}}''_{\sigma'}) Y_\ell^{\mu *}(\hat{\underline{\kappa}}^\circ)$$

$$(\times) D^{\ell *}_{m,k} D^{\ell *}_{\mu,m}(\alpha'\beta'\gamma') e^{ik(1-\rho)\alpha} | \delta n RKM \rangle .$$

Now using the orthogonality integral

$$\int d\Omega(\alpha'\beta'\gamma') D^{\ell}_{\mu';m'} D^{\ell *}_{\mu,m} = \frac{8\pi^2}{2\ell+1} \delta_{\ell\ell'} \delta_{mm'} \delta_{\mu\mu'} , \qquad (4.20)$$

and then the relation

$$\sum_{\mu} Y_l^{\mu}(\underline{\hat{R}}^0)\, Y_l^{\mu *}(\underline{\hat{R}}^0) = \frac{2l+1}{4\pi}\,, \qquad (4.21)$$

we find in the bound case

$$\langle \sigma\sigma'; \delta n RKM\rangle_{av} = \sum_{gR'K'M'} e^{i\frac{t}{\hbar}(E_{RKM}-E_{R'K'M'})}\, 4\pi \sum_{lmkk'} Q^{g\sigma\sigma'}_{lk'lk}\, S^{g}_{k'k}\, P^{lm}_{k'k}\,, \qquad (4.22)$$

where $Q^{g\sigma\sigma'}_{1k'1k}$ and $S^{g}_{k'k}$ have been defined in the previous chapter, and where

$$P^{lm}_{k'k} = \langle RKM| D^{l}_{m,k'} |R'K'M'\rangle\langle R'K'M'| D^{l*}_{m,k} |RKM\rangle. \qquad (4.23)$$

$P^{lm}_{k'k}$ can be reduced due to the form of $|RKM\rangle$ and the factored representation of $D^{l}_{m,k}$, as follows:

$$\langle RKM| D^{l}_{m,k'} |R'K'M'\rangle = N_{RKM} N_{R'K'M'} \int_0^{2\pi} d\psi\, e^{i(M'-M-m)\psi}$$

$$(\times) \int_0^{2\pi} d\varphi'\, e^{i(K'-K-k')\varphi'} \int_0^{\infty} \frac{dx}{2\eta}\, x^{\frac{|M-K|+|M'-K'|}{2}}\, e^{-x}\, L_R^{|M-K|}(x)\, L_{R'}^{|M'-K'|}(x)\, d^{l}_{m,k'}\,,$$

$$(4.24)$$

$$\langle R'K'M'| D^{l*}_{m,k} |RKM\rangle = N_{RKM} N_{R'K'M'} \int_0^{2\pi} d\psi\, e^{i(M-M'+m)\psi}$$

$$(\times) \int_0^{2\pi} d\varphi'\, e^{i(K-K'+k)\varphi'} \int_0^{\infty} \frac{dx}{2\eta}\, x^{\frac{|M-K|+|M'-K'|}{2}}\, e^{-x}\, L_R^{|M-K|}(x)\, L_{R'}^{|M'-K'|}(x)\, d^{l}_{m,k}\,.$$

Writing F for the integral on x, we have

$$\langle RKM | D^{\ell}_{m,k'} | R'K'M' \rangle = N_{RKM} N_{R'K'M'} 2\pi \delta_{M',M+m} 2\pi \delta_{K'-K,k'} F,$$

(4.25)

$$\langle R'K'M' | D^{\ell *}_{m,k} | RKM \rangle = N_{RKM} N_{R'K'M'} 2\pi \delta_{M',M+m} 2\pi \delta_{K'-K,k} F,$$

and hence

$$\langle \sigma\sigma'; \delta n RKM \rangle_{av} = \sum_{gR'K'M'} e^{i\frac{t}{\hbar}(E_{RKM} - E_{R'K'M'})} 64\pi^5 N^2_{RKM}$$

$$(\times) N^2_{R'K'M'} \sum_{\ell m k} Q^{g\sigma\sigma'}_{\ell k \ell k} S^g_{kk} F^2 \delta_{M',M+m} \delta_{K'-K,k}. \qquad (4.26)$$

In the integral F, $d^{\ell}_{m,k}$, which is defined as

$$d^{\ell}_{m,k} = G^{\ell}_{m,k} \sum_{s} g^{\ell s}_{m,k} \left(\cos\frac{\theta}{2}\right)^{2\ell+k-m-2s} \left(-\sin\frac{\theta}{2}\right)^{m-k+2s}, \qquad (4.27)$$

where

$$G^{\ell}_{m,k} = \left[(\ell+k)!(\ell-k)!(\ell+m)!(\ell-m)!\right]^{1/2},$$

(4.28)

$$g^{\ell s}_{m,k} = (-1)^s \Big/ \left[(\ell-m-s)!(\ell+k-s)!(s+m-k)!\,s!\right],$$

may be written in the small angle approximation consistent with |RKM>:

$$d^{\ell}_{m,k} \simeq (-1)^{m-k} G^{\ell}_{m,k} \sum_{s} g^{\ell s}_{m,k} e^{-\frac{\theta^2}{4}(2\ell+k-m-2s)} \left(\frac{\theta}{2}\right)^{m-k+2s}. \qquad (4.29)$$

Again set x = $\eta\theta^2$, so that

$$d^{l}_{m,k}(x) = (-1)^{m-k} G^{l}_{m,k} \sum_{s} g^{ls}_{m,k}\, e^{-\frac{x}{4\eta}(2l+k-m-2s)} \left(\frac{x}{4\eta}\right)^{s+\frac{m-k}{2}} . \tag{4.30}$$

Integral F then becomes

$$F \simeq \frac{(-1)^{m-k}}{2\eta} G^{l}_{m,k} \sum_{s} g^{ls}_{m,k} \left(\frac{1}{4\eta}\right)^{s+\frac{m-k}{2}} \int_{0}^{\infty} dx\, x^{a} e^{-(p+1)x} L^{a-b}_{R} L^{a-c}_{R'} . \tag{4.31}$$

We will denote the integral in (4.31) as follows:

$$S_{RR'}(abc;p) = \int_{0}^{\infty} dx\, x^{a} e^{-(p+1)x} L^{a-b}_{R}(x) L^{a-c}_{R'}(x) , \tag{4.32}$$

with

$$\begin{aligned} p &= \frac{1}{4\eta}(2l+k-m-2s), \\ a &= \frac{1}{2}(|M-K| + |M-K-k+m| + 2s + m - k), \\ b &= \frac{1}{2}(|M-K-k+m| - |M-K| + 2s + m - k), \\ c &= \frac{1}{2}(|M-K| - |M-K-k+m| + 2s + m - k), \end{aligned} \tag{4.33}$$

and a, b, and c are always positive integers or zero. The integral S (evaluated in Appendix I) is

$$S_{RR'}(abc;\rho)=(-1)^{R+R'}(R+a-b)!\,(R'+a-c)!$$

$$(\times)\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\frac{(-1)^{\sigma+d}\,\rho^{\sigma-d}(a+\sigma)!\,(b+\sigma-d)!\,(c+\sigma-d)!}{d!\,(\sigma-d)!\,(R'-d)!\,(R-d)!\,(b+\sigma-R)!\,(c+\sigma-R')!} \qquad (4.34)$$

with $d < \min\begin{pmatrix}R+1\\R'+1\end{pmatrix}$ and $\sigma > \max\begin{pmatrix}R-b-1\\R'-c-1\end{pmatrix}$ as conditions which guarantee the arguments of the factorials in the denominator are never negative. The selection rule on the quantum number R for a given a, b, and c is quite complex but can be derived from the above expression for the integral S.

The above equations represent a formal development of the matrix elements in which all possible transitions of the scattering material are taken into account. In view of the fact that the hindered over-all rotation model used is meaningful only if $\eta >> 1$, it is then appropriate to develop a power series expansion in inverse powers of this parameter. A natural and convenient expression for $2\eta F$ can be developed as a power series in $(1/4\eta)^{1/2}$ as suggested by (4.31):

$$2\eta F = F_0+\left(\frac{1}{4\eta}\right)^{1/2}F_1+\frac{1}{4\eta}F_2+O\left[\left(\frac{1}{4\eta}\right)^{3/2}\right]+\cdots, \qquad (4.35)$$

with

$$F_0 = \delta_{mk} \int_0^\infty d\chi \, \chi^{|M-K|} e^{-\chi} L_R^{|M-K|} L_{R'}^{|M-K|} ,$$

$$F_1 = \pm \delta_{m,k\pm 1} \sqrt{(\ell \mp k)(\ell \pm k+1)} \int_0^\infty d\chi \, \chi^{\frac{|M-K|+|M-K\pm 1|+1}{2}} e^{-\chi} L_R^{|M-K|} L_{R'}^{|M-K\pm 1|} \qquad (4.36)$$

$$F_2 = -\delta_{m,k} (\ell^2 - k^2 + 1) \int_0^\infty d\chi \, \chi^{|M-K|+1} e^{-\chi} L_R^{|M-K|} L_{R'}^{|M-K|} .$$

The double sign in F_1 denotes a sum of two terms corresponding to upper and lower signs, respectively. The various integrals in the above are particular cases of $S_{RR'}(abc;o)$ which is (see Appendix I)

$$S_{RR'}(abc;o) = (-1)^{R+R'} (R+a-b)!(R'+a-c)!\, b!\, c!$$

$$(\times) \sum_{\sigma} \frac{(a+\sigma)!}{\sigma!(R'-\sigma)!(R-\sigma)!(b+\sigma-R)!(c+\sigma-R')!} , \qquad (4.37)$$

with $\max\begin{pmatrix} R-b-1 \\ R'-c-1 \end{pmatrix} < \sigma < \min\begin{pmatrix} R'+1 \\ R+1 \end{pmatrix}$. If the condition on σ is not satsified, the integral is zero which indicates that all transitions are forbidden.

Since F appears as F^2 it will be sufficient for most cases to retain only the first two terms in the expansion of $2\eta F$. Note that in so doing, we need consider only those cases for which $m = k$, or $m = k\pm 1$. By ignoring the term of $O(1/4\eta)$ in the expansion of $2\eta F$, one can easily show that we are effectively neglecting a correction to the elastic scattering (essentially represented by F_0) of order $1/4\eta$ and a correction to inelastic scattering of order $1/16\eta^2$. We have kept dominant inelastic terms by keeping F_1, which gives rise to a first order energy exchange of $\sqrt{2\lambda A}$. Transitions involving multiples of this amount appear only in higher order terms which have been neglected because of their relatively small intensity. A transition involving an exchange of $(2\lambda A)^{1/2}$ is considered to be a hindered over-all rotation excitation.

Returning to a consideration of S^g_{kk}, we see that we may write these as in (3.117), but with $k' = k$. Thus (4.26) becomes

$$\langle\sigma\sigma';\delta nRKM\rangle_{av} = \frac{4\pi R!}{[(R+|M-K|)!]^3}\sum_{gR'K'M'} e^{\frac{it}{\hbar}(E_{RKM}-E_{R'K'M'})}\sum_{lmk} Q^{g\sigma\sigma'}_{lklk}$$

$$(\times)\, S^g_{kk}\,\delta_{M',M+m}\,\delta_{K'-K,k}\frac{R'!}{[(R'+|M-K-k+m|)!]^3}\left\{\left[F_0+\left(\frac{1}{4\eta}\right)^{1/2}F_1\right]^2\right\}. \tag{4.38}$$

For a single symmetric molecule with free internal rotation the appropriate rotational matrix elements are

$$\langle\sigma\sigma';mRKM\rangle = \langle mRKM|e^{i\underline{\kappa}\cdot\underline{b}_\sigma(t)}e^{-i\underline{\kappa}\cdot\underline{b}_{\sigma'}}|mRKM\rangle, \tag{4.39}$$

which when averaged over the random directions of the electric field become

$$\langle \sigma\sigma'; mRKM\rangle_{av} = \sum_{g m' R' K' M'} e^{i\frac{t}{\hbar}(E_{mRKM} - E_{m'R'K'M'})} 4\pi \sum_{\ell\mu k k'} Q^{g\sigma\sigma'}_{\ell k' \ell k} T^{g}_{k'k} P^{\ell\mu}_{k'k}, \tag{4.40}$$

where $T^{g}_{k'k}$ was defined in (3.145). Because of the Kronecker delta's, $\delta_{k'k}\delta_{K'-K,k}$, which arise in the evaluation of $P^{\ell\mu}_{k'k}$ as discussed in the treatment of the bound case, the T^{g}_{kk} are given by (3.146). Therefore,

$$\langle \sigma\sigma'; mRKM\rangle_{av} = \frac{4\pi R!}{[(R+|M-K|)!]^3} \sum_{g m' R' K' M'} e^{i\frac{t}{\hbar}(E_{mRKM} - E_{m'R'K'M'})}$$

$$(\times) \sum_{\ell\mu k} Q^{g\sigma\sigma'}_{\ell k \ell k} T^{g}_{kk} \delta_{M',M+\mu} \delta_{K'-K,k} \tag{4.41}$$

$$(\times) \frac{R'!}{[(R'+|M-K-k+\mu|)!]^3} \left\{ F_0^2 + \frac{1}{4\eta} F_1^2 \right\}.$$

To evaluate the "outer" scattering contributions from different molecules, we need to find

$$\langle \chi_{\substack{\ell\ell' \\ \sigma\sigma'}} \rangle = \langle {}^{\delta n}_{m}RKM | e^{i\underline{K}\cdot\underline{b}_{\ell\sigma}(t)} e^{-i\underline{K}\cdot\underline{b}_{\ell'\sigma'}} | {}^{\delta n}_{m}RKM \rangle. \tag{4.42}$$

Rather than specify a directional correlation from one molecule to another, we will average the product over orientations of the electric field separately. Then

$$\langle \chi_{\substack{\ell\ell' \\ \sigma\sigma'}} \rangle = j_0(\kappa b_{\ell\sigma})\, j_0(\kappa b_{\ell'\sigma'}). \tag{4.43}$$

As a result of the single-particle prescription for H, "outer" effects contribute to only the quasi-elastic peak.

4.4 THERMAL AVERAGE AND DIFFERENTIAL CROSS SECTION

We have evaluated the necessary matrix elements to describe the various rotational slow-neutron scattering processes on this view of the system. The present approach results in an explicit summation of all possible transitions, and consequently considerable reduction is still necessary before a particular process can be investigated in detail.

The thermal average we have to perform in the bound case can be displayed as

$$\begin{aligned}
\langle \chi^{rot}_{\sigma\sigma'} \rangle_T &= \sum_{\delta n RKM} P_{\delta n RKM} \langle \sigma\sigma'; \delta n RKM \rangle_{av}, \\
&= \frac{1}{Z} \sum_{\delta n RKM} \langle \sigma\sigma'; \delta n RKM \rangle_{av}\, e^{-\beta E_{RKM}}, \\
&= \frac{4\pi}{Z} \sum_{\ell k g RKM} W(RKM, t)\, Q^{g\sigma\sigma'}_{\ell k \ell k} \langle \chi^{g}_{k} \rangle_T,
\end{aligned} \tag{4.44}$$

where the canonical ensemble partition function is

$$Z \equiv \sum_{RKM} e^{-\beta E_{RKM}}, \tag{4.45}$$

the torsional thermal average is given by (3.136), and where

$$W(RKM,t) = \frac{R!\, e^{-\beta E_{RKM}}}{[(R+|M-K|)!]^3} \sum_{R'K'M'} e^{i\frac{t}{\hbar}(E_{RKM}-E_{R'K+k\, M+m})}$$

$$(x)\, \delta_{K',K+k} \sum_{m} \delta_{M',M+m} \frac{R'!}{[(R'+|M-K-k+m|)!]^3} \left\{ F_0^2 + \frac{1}{4\eta} F_1^2 \right\}. \tag{4.46}$$

The calculation of W(RKM,t) requires explicit determination of the integrals in F_0^2 and F_1^2 and the associated selection rules for R'. We note that

$$\begin{aligned} F_0^2 &= \delta_{mk}\, S^2_{RR'}(|M-K|,0,0;0), \\ &= \delta_{mk}\, \delta_{RR'} \frac{[(R+|M-K|)!]^6}{(R!)^2}, \end{aligned} \tag{4.47}$$

and that

$$\begin{aligned} F_1^2 = {} & \delta_{m,k+1}\, C_+ S^2_{RR'}(a'b'c';0) \\ & + \delta_{m,k-1}\, C_- S^2_{RR'}(a''b''c'';0), \end{aligned} \tag{4.48}$$

where we have used

$$C_+=(l-k)(l+k+1), \qquad C_-=(l+k)(l-k+1),$$

$$2a'=|M-K|+|M-K+1|+1, \quad 2a''=|M-K|+|M-K-1|+1,$$

$$2b'=|M-K+1|+1-|M-K|, \quad 2b''=|M-K-1|+1-|M-K|, \tag{4.49}$$

$$2c'=|M-K|+1-|M-K+1|, \quad 2c''=|M-K|+1-|M-K-1|.$$

Now we note that

(1) if M = K, then

$$a'=1, \ b'=1, \ c'=0,$$
$$a''=1, \ b''=1, \ c''=0, \tag{4.50}$$

(2) if M-K = +(|M-K|), then

$$a'=|M-K|+1, \ b'=1, \ c'=0,$$
$$a''=|M-K|, \ b''=0, \ c''=1, \tag{4.51}$$

(3) if M-K = -(|M-K|), then

$$a'=|M-K|, \ b'=0, \ c'=1,$$
$$a''=|M-K|+1, \ b''=1, \ c''=0, \tag{4.52}$$

so that

$$F_1^2(-|M-K|)=\delta_{m,k+1}C_+S^2_{RR'}(|M-K|,0,1;0)+\delta_{m,k-1}C_-S^2_{RR'}(|M-K|+1,1,0;0),$$

$$F_1^2(M=K)=\delta_{m,k+1}C_+S^2_{RR'}(1,1,0;0)+\delta_{m,k-1}C_-S^2_{RR'}(1,1,0;0), \tag{4.53}$$

$$F_1^2(+|M-K|)=\delta_{m,k+1}C_+S^2_{RR'}(|M-K|+1,1,0;0)+\delta_{m,k-1}C_-S^2_{RR'}(|M-K|,0,1;0),$$

and we need only evaluate three $S_{RR'}(abc;o)$. These are

$$S_{RR'}(|M-K|,0,1;0)=\delta_{RR'}\frac{1}{C_{|M-K|}(R+|M-K|)}+\delta_{R,R'-1}\frac{1}{C_{|M-K|}},$$

$$S_{RR'}(|M-K|+1,1,0;0)=\delta_{RR'}\frac{(R+|M-K|+1)^2}{C_{|M-K|}}+\delta_{R,R'+1}\frac{R}{C_{|M-K|}}, \tag{4.54}$$

$$S_{RR'}(1,1,0;0)=\delta_{RR'}\left[(R+1)!\right]^2+\delta_{R,R'+1}(R!)^2R,$$

where

$$C_{|M-K|}=\frac{R!}{\left[(R+|M-K|)!\right]^3}\ . \tag{4.55}$$

Hence

$$F_1^2(-|M-K|)=\delta_{m,k+1}C_+\left\{\delta_{RR'}\frac{1}{C^2_{|M-K|}(R+|M-K|)^2}+\delta_{R,R'-1}\frac{1}{C^2_{|M-K|}}\right\}$$

$$+\delta_{m,k-1}C_-\left\{\delta_{RR'}\frac{(R+|M-K|+1)^4}{C^2_{|M-K|}}+\delta_{R,R'+1}\frac{R^2}{C^2_{|M-K|}}\right\}, \tag{4.56}$$

$$F_1^2(M=K)=\left\{\delta_{m,k+1}C_+ + \delta_{m,k-1}C_-\right\}\left\{\delta_{RR'}\left[(R+1)!\right]^4+\delta_{R,R'+1}(R!)^4R^2\right\},$$

$$F_1^2(+|M-K|)=\delta_{m,k+1}C_+\left\{\delta_{RR'}\frac{(R+|M-K|+1)^4}{C_{|M-K|}^2}+\delta_{R,R'+1}\frac{R^2}{C_{|M-K|}^2}\right\} \tag{4.56}$$

$$+\delta_{m,k-1}C_-\left\{\delta_{RR'}\frac{1}{C_{|M-K|}^2(R+|M-K|)^2}+\delta_{R,R'-1}\frac{1}{C_{|M-K|}^2}\right\}.$$

Using these results for F_0^2 and F_1^2, we find

$$W(RKM,t)=\left[W_0(KM,t)+W_1(RKM,t)\right]e^{-\beta\epsilon_{RKM}}, \tag{4.57}$$

where the term

$$W_0(KM,t)=e^{-i\frac{t}{\hbar}Ak\left[\frac{I}{I_z}(2K+k)+M-K\right]}, \tag{4.58}$$

comes from F_0^2 and where the term

$$\begin{aligned} W_1(RKM,t)&=a_\pm\sum_{R'}\xi_\pm e^{i\frac{t}{\hbar}E_\pm}, \quad (K\neq M) \\ &=a_\pm\sum_{R'}\xi' e^{i\frac{t}{\hbar}E_\pm'}, \quad (K=M) \end{aligned} \tag{4.59}$$

with

$$\begin{aligned}
a_{\pm} &= (\ell \mp k)(\ell \pm k+1), \\
E_{\pm} &= E_{RKM} - E_{R'\,K+k\;M+k\pm 1}, \\
E'_{\pm} &= E_{RKK} - E_{R'\,K+k\;K+k\pm 1}, \\
\xi_{+} &= (R+|M-K|+1)\,\delta_{RR'} + R\,\delta_{R',R-1}, \\
\xi_{-} &= (R+|M-K|)\,\delta_{R'R} + (R+1)\,\delta_{R'R+1}, \\
\xi' &= (R+1)\,\delta_{R'R} + R\,\delta_{R',R-1}
\end{aligned} \qquad (4.60)$$

comes from evaluating $F_1{}^2$. In $W_1(RKM,t)$ the $\pm$ signs again imply the sum of the two terms corresponding to upper and lower signs, respectively. In $W_0(t)$, all terms with $k = o$ contribute to rotational elastic scattering where as the $k \neq o$ terms correspond to rotational transitions involving free over-all rotational energies. $W_1(RKM,t)$ accounts for hindered over-all rotational effects. We can now explicitly display

$$\langle \chi^{rot}_{\sigma\sigma'} \rangle_T = \frac{4\pi}{Z} \sum_{\ell k q} W_k(t)\, Q^{q\sigma\sigma'}_{\ell k \ell k} \langle \chi^{q}_{k} \rangle_T, \qquad (4.61)$$

where

$$W_k(t) = \sum_{R'RKM} \Big\{ \delta_{R'R} e^{i\frac{t}{\hbar}E'} + \delta_{MK} \xi' \left[a_+ e^{i\frac{t}{\hbar}E'_+} + a_- e^{i\frac{t}{\hbar}E'_-} \right] + a_+ \xi_+ e^{i\frac{t}{\hbar}E_+} + a_- \xi_- e^{i\frac{t}{\hbar}E_-} \Big\} e^{-\beta E_{RKM}} , \tag{4.62}$$

with

$$E' = E_{RKK} - E_{R\,K+k\,K+k} . \tag{4.63}$$

In principle, calculation with (4.61) and (4.62) is straight-forward and explicitly accounts for a very rich inelastic spectrum consisting of hindered over-all rotational transitions and low energy free over-all rotational transitions. However, considerable numerical work can be avoided by proceeding analytically at this point, even though this requires some approximative treatment to allow the sums over RKM to be done. Thus, we ignore the effective coupling between the hindered and free over-all rotational transitions, and write

$$\frac{1}{Z} W_k(t) = \frac{1}{Z_F Z_H} \left(\sum_{K'} e^{-i\frac{t}{\hbar}Ck(2K'+k)} e^{-\beta C K'^2} \right) \sum_{RKM} W_1(RKM,t)\, e^{-\beta E_{RKM}} \tag{4.64}$$

with

$$Z_F = \sum_K e^{-\beta C K^2},$$
$$Z_H = \sum_{Rh} e^{-\beta E_{R|h|}}. \qquad (4.65)$$

Free over-all rotational energies are neglected in $W_1(RKM,t)$ and as a first approximation in the first factor we have kept only the K = M terms, since the K ≠ M terms are much more severly attenuated by the Boltzmann factor than the terms with K = M. This treatment of $W_K(t)$ enables us to keep the effects of both the hindered and free over-all rotational motions. We note that in the summation over RKM with the free over-all rotational energies neglected, the terms are functions of h = M-K only, rather than M and K separately. Thus, the energy is

$$E_{R|h|} = \sqrt{2\lambda A}\,(2R+|h|+1)-\lambda, \qquad (4.66)$$

and the partition function Z_H is

$$Z_H = \sum_{Rh} e^{-\beta E_{R|h|}},$$
$$= \coth\left(\frac{\nu}{2}\right) e^{\beta\lambda-\nu}\left(1-e^{-2\nu}\right)^{-1}, \qquad (4.67)$$

where

$$\nu = \beta\sqrt{2\lambda A}. \qquad (4.68)$$

Then performing the R' summations, we find

$$W_1(RKM,t)=W_1(R,-|h|,t)+W_1(R,0,t)+W_1(R,+|h|,t), \quad (4.69)$$

$$\begin{aligned}W_1(RKM,t)=1&+\frac{C_+}{4\eta}\left\{(R+|h|)\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right\}\\&+\frac{C_-}{4\eta}\left\{R\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+|h|+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right\}\\&+1+\frac{C_++C_-}{4\eta}\left\{R\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right\}\\&+1+\frac{C_-}{4\eta}\left\{(R+|h|)\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right\}\\&+\frac{C_+}{4\eta}\left\{R\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+|h|+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right\}.\end{aligned} \quad (4.70)$$

Thus, the summation over h yields

$$\begin{aligned}\sum_{KM}W_1(RKM,t)\,e^{-\beta E_{RKM}}=\frac{e^{\beta\lambda-\nu}\,e^{-2\nu R}}{(1-e^{-\nu})^2}&\left\{(1-e^{-2\nu})\right.\\&\times\left[1+\frac{(C_++C_-)}{4\eta}\left(R\,e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+(R+1)\,e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right)\right]\\&\left.+\frac{(C_++C_-)}{4\eta}\,e^{-\nu}\left(e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right)\right\}.\end{aligned} \quad (4.71)$$

Finally, the sum over R can be performed with the result that

$$\frac{1}{Z}W_k(t)=\frac{1}{Z_F}\left(\sum_K e^{-i\frac{t}{\hbar}Ck(2K+k)}e^{-\beta CK^2}\right)$$
$$(\times)\left[1+\frac{\ell(\ell+1)-k^2}{2\eta(1-e^{-\nu})}\left(e^{-\nu}e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right)\right], \qquad (4.72)$$

and hence the rotational thermal average becomes simply

$$\langle \chi^{rot}_{\sigma\sigma'}\rangle_T=\frac{4\pi}{Z_F}\sum_{\ell kgK}Q^{g\sigma\sigma'}_{\ell k\ell k}\,e^{-i\frac{t}{\hbar}Ck(2K+k)}e^{-\beta CK^2}$$
$$(\times)\left[1+\frac{\ell(\ell+1)-k^2}{2\eta(1-e^{-\nu})}\left(e^{-\nu}e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}+e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right)\right] \qquad (4.73)$$
$$(\times)\,e^{-D_gk^2}\sum_{n=-\infty}^{+\infty}e^{-in\omega_T t}\left(3e^{\beta\hbar\omega_T}-2\right)^{n/2}I_n(P_gk^2).$$

The average over initial hindered over-all rotational states has been performed using all possible states, but since large R and h values are not admissible due to the restriction of the small-angle approximation, the use of all possible states is a procedure which is not entirely consistent with the hindered over-all rotation model. However, no significant error is anticipated for $\sqrt{2\lambda A} \gtrsim k_BT$, since the series is, in general, very rapidly convergent due to the rapid attenuation provided by the Boltzmann factor.

This intermediate scattering function or thermal average now describes the scattering process for symmetric molecule rotational transitions in terms of two components, the time-independent component ($\ell = k = n = o$) gives elastic effects while the time-dependent component gives inelastic effects due to low energy free over-all rotations, hindered over-all rotations, and torsional oscillations.

Before the double differential cross section can be calculated, the question of the description of the translational degrees of freedom of molecules in the liquid state must be faced. Translational motions in gases and solids are well understood but in liquids remain an active field of investigation at the moment. Simple translational-model calculations are discussed in more detail in Appendix D. Following Yip,[73] who has given an approximate treatment of translations in polar liquids, we will assume, for the present, that translational motion is hindered and can be approximately characterized by an oscillator model with a single characteristic frequency ω. This oscillator description of center-of-mass motions is clearly not unreasonable in view of observations of solid-like behavior in liquids in slow-neutron scattering studies,[110-112] but it is admittedly a crude representation of the physical situation since this description neither admits a spectrum of translational frequencies nor takes into account the fact that the oscillational states in the liquid have finite lifetimes and are subject to constant fluctuations (see Chapter V). The adoption of the oscillator model here is made for calculational convenience. A more elaborate treatment of translations might employ any of a number of different descriptions (see Appendix D), such as the collective crystalline dislocation model recently proposed by

Ookawa[113] and Rosenbaum,[114] or the stochastic model of Rahman, Singwi, and Sjolander.[115]

The translational thermal average for scattering from a single molecule in the well-known oscillator model is

$$\langle \chi^{trans} \rangle_T = e^{-D\kappa^2} \sum_{s=-\infty}^{+\infty} I_s(P\kappa^2)\, e^{s\left(\frac{\hbar\omega}{2k_BT} - i\omega t\right)}, \tag{4.74}$$

with

$$D = \frac{\hbar}{2M\omega} \coth \frac{\hbar\omega}{2k_BT},$$

$$P = \frac{\hbar}{2M\omega} \operatorname{csch} \frac{\hbar\omega}{2k_BT}, \tag{4.75}$$

and for interference scattering, we can write[93]

$$\begin{aligned} \sum_{jj'} \langle e^{i\underline{\kappa}\cdot\underline{R}_j(t)} e^{-i\underline{\kappa}\cdot\underline{R}_{j'}} \rangle_T &= \sum_{jj'} \langle e^{i\underline{\kappa}\cdot\underline{R}_j} \rangle_T \langle e^{i\underline{\kappa}\cdot\underline{R}_{j'}} \rangle_T \\ &= \sum_{jj'} e^{-D\kappa^2} e^{i\underline{\kappa}\cdot(\underline{x}_j - \underline{x}_{j'})} \\ &= \frac{d}{N} \int e^{i\underline{\kappa}\cdot\underline{R}}\, g(R)\, d^3R \end{aligned} \tag{4.76}$$

where d is the number of molecules per unit volume and g(R) is the radial distribution function.[94]

Using (3.93) for the vibrational thermal average appropriately averaged, we can now calculate the cross section, as follows

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \sum_{\sigma\sigma'} \frac{k_f}{k_i}\frac{a_{\sigma\sigma'}}{2\pi\hbar}\int dt\, e^{-i\epsilon\frac{t}{\hbar}} \Bigg\{ \frac{4\pi}{Z_F}\, e^{-D\kappa^2} \sum_{s=-\infty}^{+\infty} I_s(P\kappa^2)\, e^{s(\frac{\beta}{2}\hbar\omega - i\omega t)}$$

$$(x)\, e^{-\kappa^2\gamma_{\sigma\sigma'}} \sum_{lkg} Q^{g\sigma\sigma'}_{lklk} \Bigg[1 + \frac{l(l+1)-k^2}{2\eta\left(1-e^{-\beta\sqrt{2\lambda A}}\right)}\left(e^{-\beta\sqrt{2\lambda A}}\, e^{i\frac{t}{\hbar}\sqrt{2\lambda A}}\right.$$

$$\left. + e^{-i\frac{t}{\hbar}\sqrt{2\lambda A}}\right)\Bigg] e^{-D_g k^2} \sum_{n=-\infty}^{+\infty} e^{-in\omega_T t}\left(3e^{\beta\hbar\omega_T}-2\right)^{n/2} I_n(P_g k^2) \tag{4.77}$$

$$(x) \sum_{K} e^{-i\frac{t}{\hbar}Ck(2K+k)}\, e^{-\beta CK^2} + e^{-\kappa^2\gamma_{\sigma\sigma'}}\, j_0(\kappa b_\sigma)\, j_0(\kappa b_{\sigma'})\, \frac{d}{N}\int d^3R\, e^{i\underline{\kappa}\cdot\underline{R}}\, g(R) \Bigg\}$$

which, by performing the indicated integration, becomes

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \frac{4\pi}{Z_F}\sum_{\sigma\sigma'} a_{\sigma\sigma'} \Bigg[\sqrt{\frac{E_f}{E_i}}\, e^{-\kappa^2(\gamma_{\sigma\sigma'}+D)} \sum_{s=-\infty}^{+\infty} e^{s\frac{\beta}{2}\hbar\omega}\, I_s(P\kappa^2) \tag{4.78}$$

$$\otimes \sum_{\ell g} \left\{ \left[Q^{g\sigma\sigma'}_{\ell 0 \ell 0} \left\{ \sum_{K=-\infty}^{+\infty} e^{-\beta C K^2} \right\} \left\{ \delta(E_1) + C_{\ell 0} \left[\delta(E_2) e^{-\beta\sqrt{2\lambda A}} + \delta(E_3) \right] \right\} \right. \right.$$

$$+ \sum_{k=1}^{\ell} Q^{g\sigma\sigma'}_{\ell k \ell k} e^{-D_g k^2} \sum_{n=-\infty}^{+\infty} \left(3e^{\beta\hbar\omega_T} - 2\right)^{n/2} I_n(P_g k^2) \tag{4.78}$$

$$\otimes \sum_{K=-\infty}^{+\infty} e^{-\beta C K^2} (2-\delta_{K0}) \left\{ \delta(E_4) + C_{\ell k} \left[\delta(E_5) e^{-\beta\sqrt{2\lambda A}} + \delta(E_6) \right] \right\} \Bigg] \Bigg\}$$

$$\left. + \delta(\epsilon) e^{-\kappa^2 \gamma_{\sigma\sigma'}} j_0(\kappa b_\sigma) j_0(\kappa b_{\sigma'}) \frac{d}{N} \int d^3R\, e^{i\boldsymbol{\kappa}\cdot\mathbf{R}} g(R) \right] \Big\} ,$$

where

$$E_1 = \epsilon + s\hbar\omega , \qquad D_g = \tfrac{1}{2} G R_1^g(\rho) f_1(T),$$

$$E_2 = E_1 - \sqrt{2\lambda A} , \qquad P_g = 2 G R_2^g(\rho) f_2(T),$$

$$E_3 = E_1 + \sqrt{2\lambda A} ,$$

$$E_4 = E_1 + n\hbar\omega_T + Ck^2 + 2KCk , \tag{4.79}$$

$$E_5 = E_4 - \sqrt{2\lambda A} ,$$

$$E_6 = E_4 + \sqrt{2\lambda A} ,$$

$$C_{\ell k} = \frac{\ell(\ell+1) - k^2}{2\eta\left(1 - e^{-\beta\sqrt{2\lambda A}}\right)} .$$

Now we turn our attention to the case of free internal rotation in the presence of hindered over-all rotation. The thermal average is

$$\langle \chi^{rot}_{\sigma\sigma'}\rangle_T = \frac{1}{Z}\sum_{mRKM}\langle\sigma\sigma';mRKM\rangle_{av}\, e^{-\beta E_{mRKM}},$$

$$= \frac{4\pi}{Z}\sum_{\ell kgmRKM} Q^{g\sigma\sigma'}_{\ell k\ell k}\, U(RKM,t)\, T^{g}_{kk}, \tag{4.80}$$

where

$$U(RKM,t) = \frac{R!\, e^{-\beta E_{mRKM}}}{\left[(R+|M-K|)!\right]^3}\sum_{R'K'M'm'} e^{i\frac{t}{\hbar}(E_{mRKM}-E_{m'R'K'M'})}$$

$$(\times)\,\delta_{K',K+k}\sum_{\mu}\delta_{M',M+\mu}\frac{R'!}{\left[(R'+|M-K-k+\mu|)!\right]^3}\left\{F_0^2+\frac{1}{4\eta}F_1^2\right\}, \tag{4.81}$$

$$Z \equiv \sum_{mRKM} e^{-\beta\left[AJ(J+1)+(C-A)K^2+F(m-\rho K)^2\right]}, \tag{4.82}$$

and T^{g}_{kk} is given by (3.150). Recall that F in (4.82) is a rotational constant. Using (4.47) and (4.56) with μ instead of m, we find

$$\mathcal{U}(RKM,t)=\left[\mathcal{U}_0(KM,t)+\mathcal{U}_1(RKM,t)\right]e^{-\beta E_{mRKM}}, \qquad (4.83)$$

where the term

$$\mathcal{U}_0(KM,t)=e^{-i\frac{t}{\hbar}F(\rho^2k^2+2\rho^2Kk+2\rho Km-m^2)}\sum_{m'}e^{i\frac{t}{\hbar}F\left[2\rho(K+k)m'-m'^2\right]}, \qquad (4.84)$$

comes from F_0^2 and where the term

$$\begin{aligned}\mathcal{U}_1(RKM,t)&=a_\pm\sum_{R'm'}\xi_\pm e^{i\frac{t}{\hbar}E_\pm^F}, \quad (K\neq M)\\ &=a_\pm\sum_{R'm'}\xi' e^{i\frac{t}{\hbar}E_\pm^{F'}}, \quad (K=M)\end{aligned} \qquad (4.85)$$

with

$$\begin{aligned}E_\pm^F&=E_{mRKM}-E_{m'R'K+k\ M+k\pm1},\\ E_\pm^{F'}&=E_{mRKK}-E_{m'R'K+k\ K+k\pm1},\end{aligned} \qquad (4.86)$$

comes from evaluating F_1^2.

As in the bound case at this stage, calculation with (4.80) through (4.86) is straightforward, in principle, but requires substantial numerical work. If we again seek to proceed analytically through some approximation, we would be forced to a more severe approximation here because unlike the bound case the energy involves free axial over-all rotation quantum numbers. Since no comparison with experiment is contemplated here for this case, we will not pursue any approximation further.

4.5 TOTAL SCATTERING CROSS SECTION

In Section 3.6, we discussed the total scattering cross section of freely rotating symmetric molecules which have an internal rotational degree of freedom. In this section, we will discuss very briefly the total cross section of symmetric molecules whose over-all rotations are hindered and which possess an internal rotational degree of freedom.

The appropriate rotational wave functions are now

$$|i\rangle = |\delta n RKM\rangle = N_{nRKM}\, e^{iM\psi} e^{iK\varphi'} x^{\frac{|M-K|}{2}} e^{-\frac{x}{2}} L_R^{|M-K|}(x)\, M_{\delta n K}(\alpha), \qquad (4.87)$$

where M(α) are the general Mathieu functions which again can be expanded in a Fourier series as in (3.215). The argument follows precisely as in Section 3.6 to yield

$$\sigma_T(E_i) = \frac{1}{k_i N} \sum_{\delta n R K M} P_{\delta n R K M} \sum_{\delta' n' R' K' M'} k_f\, \nu_0^2(\delta,\delta', n, n', K, K')\, \sigma_T^{HR}(RKM, R'K'M'), \qquad (4.88)$$

where $\nu_0^{\,2}$ is given in (3.224) and (3.232) and σ_T^{HR}(RKM,R'K'M') is the partial differential cross section of an atom in a (rigid) hindered rotator undergoing a transition from |RKM> to |R'K'M'> integrated over all $\Omega(\psi\theta\varphi)$.

Thus the qualitative argument concerning the effect of the internal rotational degree of freedom given for freely rotating molecules holds here also, where the hindrance of over-all rotation effects only one degree of freedom.

4.6 COLD-NEUTRON SCATTERING FROM LIQUID METHANOL

In this section we compare calculations based on the theory developed in the previous sections with experimental results on a substance for which appropriate measurements have been made. Liquid methanol, or methyl alcohol, CH_3OH, whose molecular electric dipole moment[116] is 1.7D is probably the simplest representative of the class of substances for which the theory is intended, although it is not strictly a member of the class because its molecules are asymmetric rather than symmetric. Nevertheless, because it has received some experimental attention, we will use the theory to calculate energy distributions for liquid CH_3OH and these will be directly compared with the measured distributions for two different scattering angles. Moreover, since liquid CH_3OH is a prime example of hydrogen-bonding association in which the polymers associate with O-H...O structures, we may test the assumption that the only effect of this bonding on internal rotation is to change the barrier height. In this regard, companion calculations and measurements of the differential cross section for liquid methyl mercaptan CH_3SH($\underline{\mu}$ = 1.26D), which is similar in structure but in which hydrogen bonding is believed not to occur, may be valuable.

Several investigators have reported neutron scattering measurements from liquid CH_3OH. Nasuhoglu and Ringo,[35] Janik,[117] and Borowski and Rzany,[118] have measured the total scattering cross section, while Brugger and Evans,[36] and Saunderson and Rainey,[37] have measured energy distributions at several different angles. No recourse to a theory including the internal rotation was available in any of these studies. The dynamics of CH_3OH molecules have been extensively studied by the optical techniques of infrared and Raman spectroscopy and results of the early work are summarized in Herzberg.[38] The frequencies of the various vibrational modes have thus been measured and compared in both vapor and liquid phases, the latest work being that of Falk and Whalley.[119] The cold neutron scattering data of Saunderson and Rainey are more sensitive to the lower energy transitions associated with translational, and internal and overall rotational motion of the molecules.

In calculating the differential cross section for CH_3OH, we follow Dennison and co-workers[76,77] and neglect the slight asymmetry introduced by the light hydrogen of the hydroxyl group (the moment of inertia ellipsoid has an asymmetry parameter which differs from 1 by only 2%). The structure of CH_3OH is summarized as: $r_{CH} = 1.093\text{Å}$, $r_{CO} = 1.421\text{Å}$, $r_{OH} = .95\text{Å}$, the oxygen atom is displaced .084Å from the symmetry axis of the CH_3 group, $\sphericalangle$ COH = 110°15', and $\sphericalangle$ HCH = 109°28'. The following consistent set of moments of inertia and rotational constants can then be used

$$I = 34.281 \times 10^{-40} \text{ gm cm}^2, \qquad A = B = .101 \text{ mev},$$

$$I_z = 6.546 \times 10^{-40} \text{ gm cm}^2, \qquad C = .528 \text{ mev},$$

$$I_a = 1.236 \times 10^{-40} \text{ gm cm}^2, \qquad F = 3.44 \text{ mev}.$$

We also deduce the distances:

$$b_{H_3} = 1.605\text{Å}, \qquad b_H = .97\text{Å},$$

$$b_O = .694\text{Å}, \qquad b_C = .727\text{Å}.$$

We will initially take the torsional oscillation frequency to have the gas phase value of 33 mev, although we might expect that the value would change somewhat in the liquid.

Two parameters in the present description, the oscillation frequency of the centers of mass and the magnitude of the local electric field, are to be estimated. Yip[73] has given an approximate criterion for the validity of the oscillator approximation in terms of the Stockmayer potential parameters ϵ and σ, and the mean separation s, between molecules at a given temperature (which may be obtained from the radial distribution function), viz., if

$$\gamma_p = \frac{.4\sigma^6}{s^6\left(1+\frac{3}{8}\frac{\mu^4}{\epsilon\sigma^6 k_B T}\right)} > .05\ , \tag{4.89}$$

the potential may be approximated by a parabola. The Stockmayer potential parameters from viscosity data[120] are $\epsilon/k_B = 570°\text{K}$, $\sigma = 3.6\text{Å}$, which when combined with $s = 4\text{Å}$ from the CH_3 to CH_3 distance in liquid methanol,[121] give a value of $\gamma_p \simeq .06$. A first estimate of the frequency is then

$$\omega = \sqrt{\frac{8\epsilon C C_1}{Ms^2}\left[22C_1 + 5(1+C_2)\right]}\ , \tag{4.90}$$

where

$$C_1 = \left(\frac{\sigma}{s}\right)^6 ; \quad C_2 = \frac{3\mu^4}{8\epsilon\sigma^6 k_B T}\ , \tag{4.91}$$

and where C is the liquid coordination number at a given temperature. Estimating C to be 8, we find $\hbar\omega \simeq 10$ mev.

The local electric field produced by the neighboring molecules can be estimated, in principle, from the structure of solid CH_3OH. However, we will estimate $E = 15 \times 10^5$ dynes/esu which is the same order of magnitude as for water.[73] Then the energy of hindered over-all rotation, $\sqrt{2\lambda A}$, is about 18 mev.

The appropriate nuclear scattering amplitudes of hydrogen, oxygen, and carbon are[122] $D_H^2 = 6.53$ barns, $A_H^2 = .18$ barns, $D_O^2 = A_O^2 = .34$ barns, $D_C^2 = A_C^2 = .41$ barns. On the basis of the scattering amplitudes, hydrogen effects constitute about 98 percent of the total scattering, and the contribution from "inner" scattering is found to be less than 2 percent and hence is ignored.

The zero-point vibrational constant is, in principle, determinable from a normal coordinate analysis and the infrared measured vibrational frequencies. However, a normal coordinate analysis of CH_3OH has not been reported. An approximate value can be found by extrapolation of the vibrational constant of ethane. We choose $\gamma_{\sigma\sigma'} = .0093\text{Å}^2$.

To compare with the Saunderson and Rainey data the cross section of Equation (4.78) must be averaged over two normalized experimental resolution functions [see Equation (2.11)], one for the incident spectrum which is triangular in energy up to the beryllium cutoff, and one for the analyzer and detector which will be assumed to be Gaussian. The effect of decreasing resolution with increasing energy is included by allowing the width of the Gaussian to increase with energy.

In Fig. 6, we compare the calculated and measured cross sections for 90° scattering. The calculated cross section has been normalized at the quasielastic peak. The combination of a rich, closely spaced inelastic spectrum and lack of resolution sufficient to resolve the many transitions produces a band-like spectrum of rotations, as tentatively assigned by Saunderson and Rainey. The major difference in the two cross sections is for energy transfers of less than 10 mev where the theory has probably not properly accounted for translational effects, low energy rotational effects, or polymer effects. The reasonable agreement obtained at larger energy transfers indicate that transitions involving both the internal rotation and the hindered whole-body rotations are significant. The calculations were performed with $0 \leftarrow 1$ and $0 \leftarrow 2$ transitions of the torsional oscillator and a torsional oscillator frequency of $\hbar\omega_T = 36$ mev. In contrast to the small effect seen in the experiment on gaseous ethane in Section 3.7, the internal rotation is seen to have a large effect here.

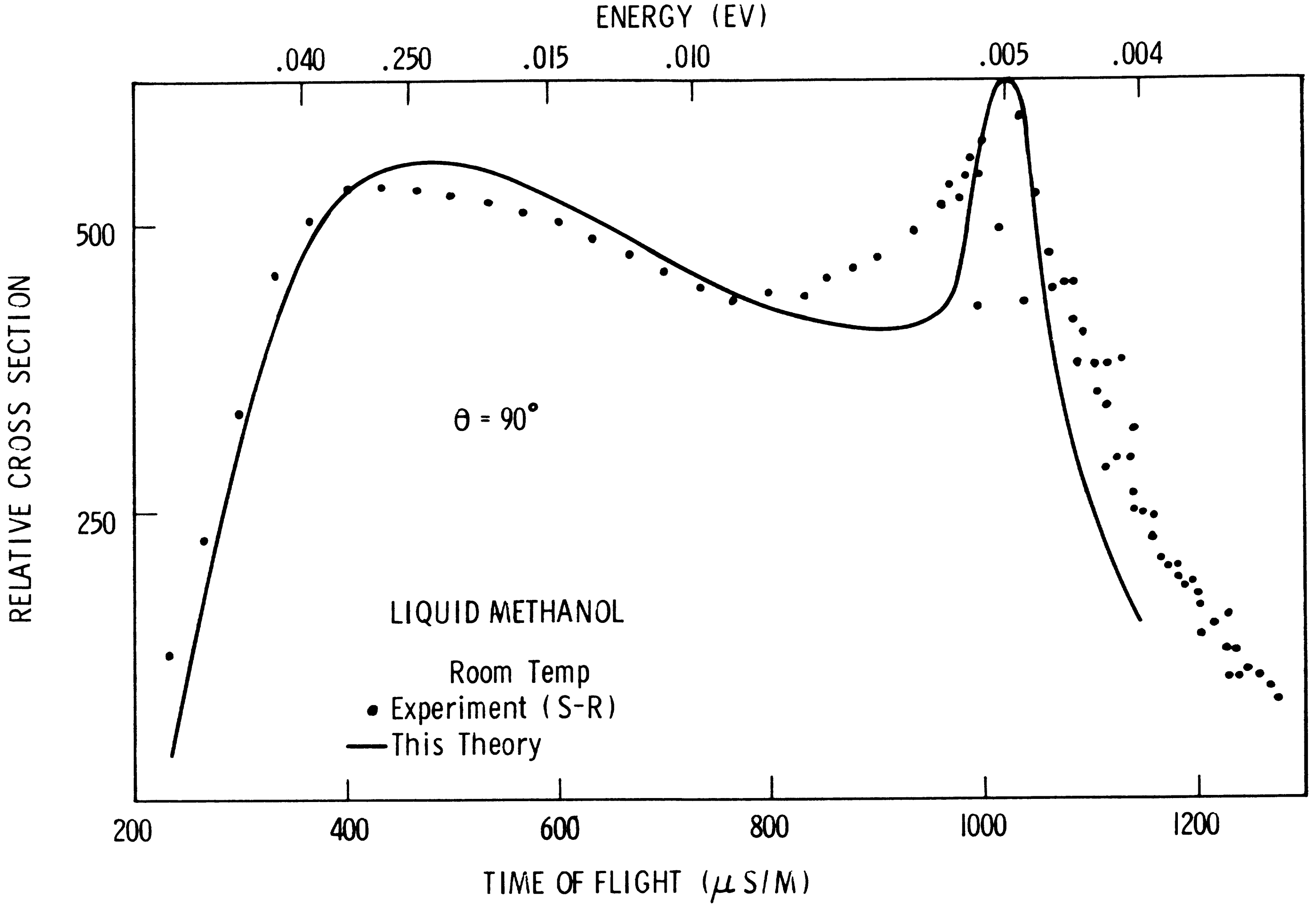


Figure 6. Relative differential scattering cross section of liquid methanol at a scattering angle of 90°.

The angular dependence of the theory is compared in Fig. 7, where the cross sections for 20° scattering are shown. No normalization was made relative to that for 90° scattering. The small energy transfer region is in somewhat closer agreement for the 20° angle. It is observed that both the theoretical intensities for inelastic scattering and the angular dependence of the theory are in reasonable agreement with experiment, which is encouraging in view of the crudeness of the oscillator description of translation, the fact that the CH_3OH molecule is asymmetric, and the other assumptions and approximations made.

In view of the data presented by Saunderson and Rainey for liquid ethanol and n-amyl alcohol which has an appearance at both 20° and 75° similar to the methanol data, it is tempting to apply this model. However, some reservations must be made in any such attempt.

First, the internal rotation of the hydroxyl group in both of these molecules is not in threefold barriers of equal height, since one of the minima is deeper than the other two. Also, the CH_3 group sees a barrier to internal rotation which is different than that seen by the hydroxyl group, so that two internal barriers are present and interact to some extent. Second, the simple model we have employed ascribing the hindering of over-all rotations to electrostatic dipole and hydrogen bonding effects is really only applicable to liquids whose molecules are small so that the local field and "ideal" dipole interaction is valid. The n-amyl alcohol molecule is becoming "large" in that its length is appreciably longer than the largest dimension of the free volume it has for rotation.

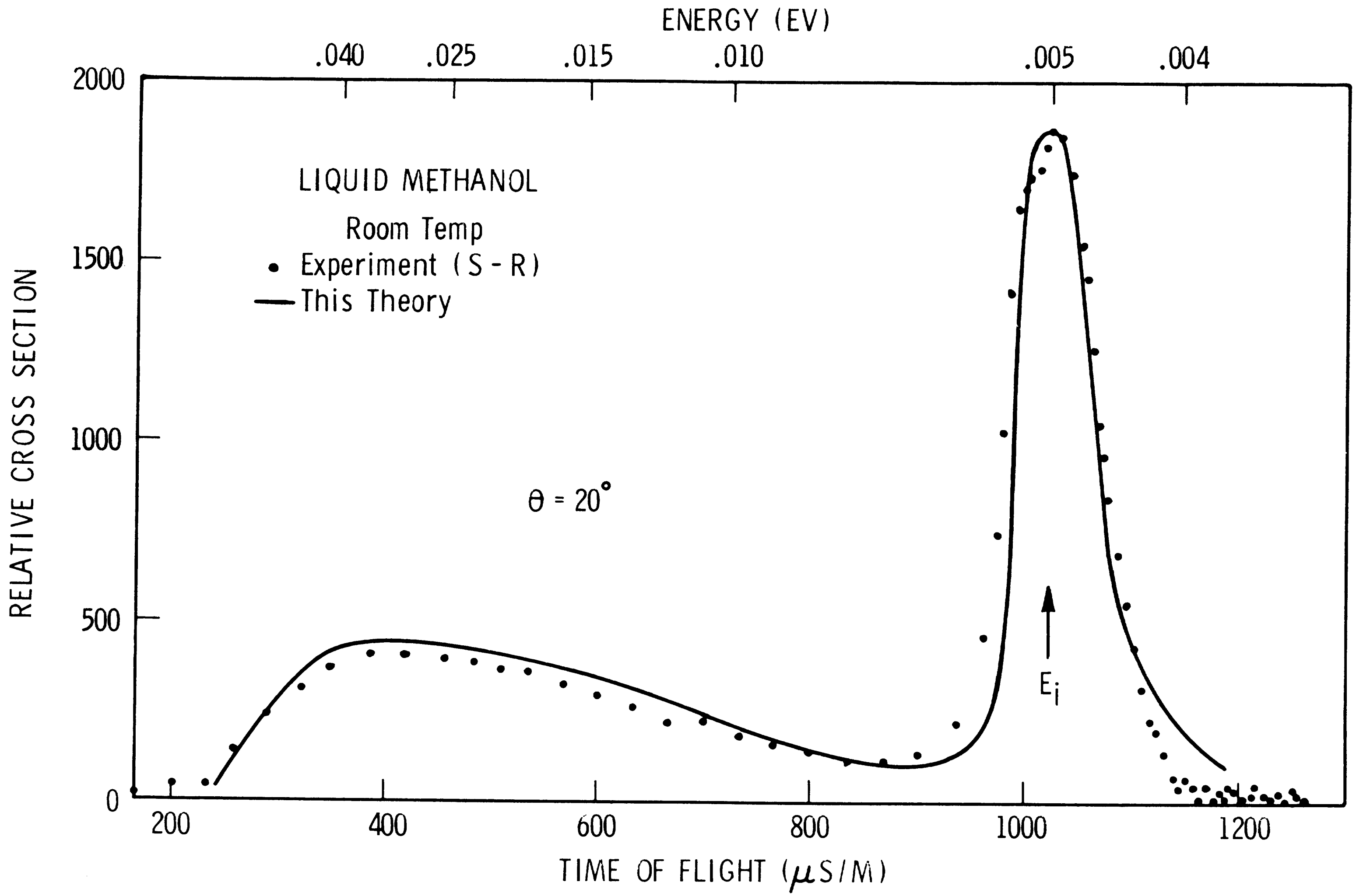


Figure 7. Relative differential scattering cross section of liquid methanol at a scattering angle of 20°.

CHAPTER V

ROTATIONAL LINE SHAPE IN SLOW-NEUTRON SCATTERING BY DIATOMIC LIQUIDS

> "The effort really to see and really to represent is no idle business."
>
> Henry James

5.1 INTRODUCTION

Although reviewing a general line shape formulation of slow-neutron scattering based on the damping theory in Chapter II, we employed only the simpler zero-line-width-and-shift limit in the discussion of internal rotation because the interpretation of the experimental data did not require the refinements of the more detailed line shape formulation. The effective coupling of internal rotational and free axial over-all rotational transitions, in fact, gave rise to effectively band-like spectra rather than measurable "line" spectra, although, in principle, the discreteness of the rotational spectra was preserved. Thus the simpler formalism which describes the positions and intensities of the transition "peaks" or lines, but not their detailed shape, was sufficient. Here, however, we may take advantage of the fact that linear molecules display neither internal rotation nor free rotation about their axis,[106] thus in polar liquids composed of such molecules a hindered rotational "line" may appear in the spectra whose "shape" is experimentally definable and may yield information on intermolecular forces and local structure. That is, by considering liquids of linear, polar molecules we can eliminate the complexity of the spectra and hence employ the full line shape formalism to advantage. This chapter reports the first application of this line shape theory to liquids.

As discussed in the preceding chapter, the rotational motion of polar molecules even in relatively simple molecular liquids whose temperature is not too high consists essentially of rotational oscillations about equilibrium orientations, which are determined by the action of the surrounding molecules and changed sharply from time to time. The duration or lifetime τ of a certain equilibrium orientation must be large compared with the period τ_p of rotational oscillations and is connected with the period by relations of the same type as occur for translational motion of molecules of the liquid,[123] viz.,

$$\tau = \tau_p e^{E_a/k_B T} \tag{5.1}$$

where E_a is the activation energy required to change the arrangement of the surrounding molecules so that a sharp change in the orientation of the central molecule results. In the limit of high temperatures as $k_B T$ becomes comparable to E_a, the rotational motion of the molecules changes to a free rotation of the same kind as in the gaseous state, thus as $k_B T \to E_a$, the appropriate time average of the local field $\underline{E}$ must approach zero. But the translational motion need not simultaneously become free. The difference between rotational and translational motion of molecules in liquids is, from this point of view, simply that in the case of translational motion the equilibrium positions of the molecules, irrespective of molecular size, are shifted by very small amounts, while in the case of rotational motion the equilibrium orientations, at least of small molecules, are rotated through large—not small—angles. However, the details of the mechanism of such reorientation processes and the effective number of molecules involved in them, are not yet clearly understood. In particular, it is not clear to what extent the changes of orientation are connected with changes of position of the central molecule.

It is the aim of this chapter to explore this problem, rather more qualitatively than quantitatively, through examination of the line width and shift contributions of a potential function, $V(\underline{R}_\ell,\theta_i)$, which depends on both the molecular center-of-mass position coordinate $\underline{R}_\ell$ and the Euler angles θ_i specifying molecular orientation. We will be guided by the hope of achieving some insight into the problem in terms of physical quantities which we can only estimate rather crudely due to a lack of experimental data. Our purpose in so doing is to discover if such insight as we can gain will stimulate and perhaps define an experiment.

5.2 THE WIDTH AND SHIFT

The function Γ defined in (2.14) is used in finding both the width γ_{fi} and shift S_{fi} also defined in (2.14). The matrix element $|\langle n|V^n+H'|n_i\rangle|^2$ appearing in the definition of Γ can be written as follows

$$\frac{1}{L^6}\left|\mathcal{V}^n_{ji}(\underline{\kappa})\right|^2 + \frac{2}{L^3}\,\mathrm{Re}\,\mathcal{V}^n_{ji}(0)H'_{ji}\,\delta(\underline{k}_i-\underline{k}_f) + \left|H'_{ji}\right|^2\delta(\underline{k}_i-\underline{k}_f),$$

where $\mathcal{V}^n(\underline{\kappa})$ is the Fourier transform of $V^n(r)$, that is,

$$\mathcal{V}^n(\underline{\kappa}) = \frac{1}{L^3}\int d^3r\, e^{i\underline{\kappa}\cdot\underline{r}}\, V^n(\underline{r}), \tag{5.2}$$

Since

$$V^n(\underline{r}) = \frac{2\pi\hbar^2}{m}\sum_{\ell\alpha} a_{\ell\alpha}\,\delta(\underline{r}-\underline{R}_{\ell\alpha}) \tag{5.3}$$

we find

$$\mathcal{V}^n(\underline{\kappa}) = \frac{2\pi\hbar^2}{mL^3}\sum_{\ell\alpha} a_{\ell\alpha}\, e^{i\underline{\kappa}\cdot\underline{R}_{\ell\alpha}}, \tag{5.4}$$

where $\underline{\kappa} = \underline{k}_i - \underline{k}_f$. The matrix elements $\langle j|\,\mathcal{V}^n(0)\,|i\rangle$ are proportional to δ_{ji} since $\mathcal{V}^n(0)$ is independent of the position coordinates $\underline{R}_{\ell\alpha}$, but there is no contribution to the width and shift from this term, since the summation in (2.14) excludes the only nonvanishing element. Thus we can split Γ into two parts,

$$\Gamma = \Gamma^n + \Gamma^m, \tag{5.5}$$

where Γ^n represents the broadening and shift due to transitions caused by neutrons and Γ^m represents the width and shift due to transitions caused by H':

$$\Gamma^n_{n_i} = \langle n_i | V^n | n_i \rangle - \sum_{n \neq n_i} \frac{|\langle n | V^n | n_i \rangle|^2}{E_n - E_{n_i} + i\epsilon},$$

$$\Gamma^m_i = \langle i | H' | i \rangle - \sum_{j \neq i} \frac{|\langle j | H' | i \rangle|^2}{E_j - E_i + i\epsilon}. \qquad (5.6)$$

Because we expect the perturbation to have a much larger effect on transitions than the neutrons, we will concentrate entirely on Γ^m. We now assume a position-orientation dependent potential form for the perturbation,

$$H' = \sum_{\ell} V_\ell(\underline{R}_\ell, \theta_i), \qquad (5.7)$$

so that the required matrix elements entering Γ^m_i are of the form,

$$\langle \psi^j_{tr} | \langle \psi^j_{rot} | V_\ell(\underline{R}_\ell, \psi\theta) | \psi^i_{rot} \rangle | \psi^i_{tr} \rangle.$$

In order to explore a possible form for V_ℓ, consider the part of the Stockmayer potential which represents the interaction between two rigid, point dipoles:

$$U_\ell^d = \frac{\underline{\mu}_\ell \cdot \underline{\mu}_i}{r_{i\ell}^3} - \frac{3(\underline{\mu}_\ell \cdot \underline{r}_{i\ell})(\underline{\mu}_i \cdot \underline{r}_{i\ell})}{r_{i\ell}^5}, \qquad (5.8)$$

with $\underline{r}_{i\ell} = \underline{R}_i - \underline{R}_\ell$. This orientation-dependent potential can be written including the effect of all the surrounding molecules as,

$$U_\ell^d = \underline{\mu}_\ell \cdot \underline{Q}, \qquad (5.9)$$

where the effective field $\underline{Q}$ is given by

$$Q_k = \sum_i \left[\frac{\mu_{ik}}{r_{i\ell}^3} - \frac{3(\underline{\mu}_i \cdot \underline{r}_{i\ell}) r_{i\ell k}}{r_{i\ell}^5} \right]. \qquad (5.10)$$

If we now expand $\underline{Q}$ in a Taylor series about the "equilibrium" position of the ℓ^{th} molecule, $\underline{R}_\ell^e$, keeping two terms we find

$$Q_i = Q_i(\underline{R}_\ell^e) + \sum_k r_k \frac{\partial Q_k(\underline{R}_\ell^e)}{\partial r_i}, \qquad (5.11)$$

where now $\underline{r} = \underline{R}_\ell - \underline{R}_\ell^e$. The first term in (5.11) can be identified as the local electric field $\underline{E}$ introduced in Chapter 4 and the second term may be thought of as a specific perturbation $V_\ell^o(\underline{R}_\ell, \theta_i)$ which couples translational and orientation-dependent effects. Just as $\underline{E}$ was taken to be uniform in the immediate vicinity of the molecule and constant over an "order interval" of time, the field gradient $\xi_{ki} = \partial Q_k / \partial r_i$ will likewise be so taken. Since all the molecules in the sample have the same dipole moment,

$$V_\ell^0(\underline{\xi}_\ell, \psi\theta) = \sum_{i,j} \mu_i r_j \xi_{ji}, \tag{5.12}$$

where i and j run over (1,2,3). But we wish to represent this energy in the laboratory coordinate system. The vector $\underline{r}$, specified in the space-fixed system, is the displacement vector of the molecule from its "equilibrium" position. The electric dipole moment $\underline{\mu}$ is specified in the molecule-fixed system so that a rotation must be performed which then expresses $\underline{\mu}$ in terms of the Euler angles and rotates ξ into diagonal form. As a zero-order approximation we will consider only V_ℓ^0. A first-order approximation might involve an additional perturbation obtained from the θ^3 and θ^4 dependent terms neglected in the strong field description and others. In that case Equation (4.5) expanded in powers of θ keeping terms through θ^4 which are of the first order in $1/\eta$, gives

$$V_\ell^1(\theta) = -\frac{2x^2}{45\eta}\frac{d}{dx} + \frac{x^2}{12\eta}, \tag{5.13}$$

where $x = \eta\theta^2$. This term is expected to be small and contribute solely to the shift to first order. It is less interesting at this point since it is position independent. In order to estimate the translational contribution, consider the following conceptual model. The rotational states used in finding the rotational contributions are pictured as being formed locally by the intermolecular forces producing a short-range ordering which is represented by the local electric field $\underline{E}$. These states are then thought to "decay" as the thermal fluctuations destroy the local ordering through rearrangements of neighboring molecules. The local structure also affects the translational motion, so the nature of the translational motion can also change when rearrangement occurs. That the effect need not be simultaneous on rotation and translation can be seen by the fact that the ordering of the local structure plays a role in determining $\underline{E}$, which affects rotation, whole the presence of near neighbors creates a type of "cage" which affects translation.

Compatible with this "quasi-crystalline" picture we choose to characterize the initial translational state as a bound state and for simplicity to take an oscillator ground state wave function as the initial translational wave function. We also choose as a representative intermediate bound state the first excited oscillator state. Finally we choose to characterize another intermediate translational state as a "gas-like" state corresponding to the presence of "holes" and the breakup of the local structure sufficient to allow the central molecule to escape its "cage."

For convenience we will also assume that the initial rotational state is a hindered rotational state, but that the intermediate rotational states are free rotational states.

The conceptual model described above does not include any specific mechanism for the formation of these locally ordered structures because no mechanism suggests itself. Thus, we are investigating the role of the lifetime of the states without saying anything about the "birth" process. Also, other than attributing the decay of the states to rearrangements which sufficiently affect short-range ordering, no mechanism for giving energy to the central molecule is described by this model.

In the first case, we are limited to discussing the initial state width and shift, since these quantities require a knowledge of only the relaxation from short-range ordering. In the second case, in order to have conservation of energy, the discrete states must be "imbedded" in the continuum states. The width and shift then become

$$\begin{aligned} \gamma &= \left| \mathrm{Im} \lim_{\epsilon \to 0^+} (-\Gamma_i) \right| , \\ \delta &= \mathrm{Re} \lim_{\epsilon \to 0^+} (-\Gamma_i) . \end{aligned} \tag{5.14}$$

Now recall that Equation (2.21) expresses the cross section as a weighted superposition of a series of Lorentzian distributions, each with different widths and shifts. For a given final state, the thermal average of these Lorentzian distributions gives a peaked curve which corresponds to the observed line in the scattered neutron spectrum. Although the individual distributions have a Lorentzian shape, their thermal average will not, in general, be a Lorentzian distribution. However, as an approximation, one may replace the resultant curve by a Lorentzian distribution with an average width and shift (this corresponds to replacing the average of a function by the function of the averaged variables). This approximation is justified when the widths of the individual Lorentzian distributions corresponding to different initial states are large compared with their shifts.[3] If this is not the case, the experimental width will be dominated by the statistical spread in the locations of the narrow Lorentzian distributions. To include the statistical broadening in an approximate way, the variance σ_s^2 of S_{fi} may be added to the square of the average width $\overline{\gamma}^2$ in the denominator of a Lorentzian distribution. This approximation is called the statistical approximation.[3]

However, the method we have described above, while appropriate to calculating a width from which an average lifetime of the states and hence of short-range ordering may be found, is not precisely the correct method for calculating the shifts. The subtle point here is that the shifts which should enter the description are those which account for the fluctuations in the states due to fluctuations in arrangements of molecules of the surroundings causing the magnitude of the local field to fluctuate around its most probable value. The shift we are calculating is rather a simple correction to the energy level. With the assumption of a distribution function describing the probability of a given field strength as a function of temperature the appropriate shifts could be crudely estimated and the temperature dependence included in the description. However, the present experimental situation probably does not warrant this elaboration, and hence having pointed out a method for estimating the shifts if so desired, we proceed to calculate only the width.

Since $\langle r\rangle = 0$ in the ground state of an oscillator, the function Γ_i is given by the intermediate state sum, where the intermediate states are of two kinds, bound and free:

$$\Gamma_i = -\sum_{n'R'M'} \frac{|\langle n'R'M'|H'|nRM\rangle|^2}{E_{n'}+E_{R'M'}-E_n-E_{RM}+i\epsilon} - \sum_{\underline{k}J'M'} \frac{|\langle \underline{k}J'M'|H'|nRM\rangle|^2}{E_{k}+E_{J'}-E_n-E_{RM}+i\epsilon}, \qquad (5.15)$$

where we have chosen n = R = M = 0 and n' = 1, and hence

$$\Gamma_i = -\sum_{R'M'} \frac{|\langle 1R'M'|H'|000\rangle|^2}{\hbar\omega+E_{R'M'}-E_{RM}+i\epsilon} - \sum_{J'M'}\left(\frac{L}{2\pi}\right)^3\int \frac{d^3k\,|H'_{\underline{k}J'M',000}|^2}{E_k+AJ'(J'+1)+i\epsilon}, \qquad (5.16)$$

and the width becomes

$$\gamma = \pi\sqrt{2}\left(\frac{M}{\hbar^2}\right)^{3/2} E_k^{1/2}\left(\frac{L}{2\pi}\right)^3 \sum_{J'M'} |H'_{\underline{k}J'M',000}|^2 \Big|_{E_{k}=AJ'(J'+1)}, \qquad (5.17)$$

where M, the mass of the molecule, is not to be confused with M', a rotational quantum number.

In considering the rotational matrix elements of H', we find that to first order in $(1/\eta)^{1/2}$ the only nonvanishing matrix element involves

$\mu_z = \mu \cos \theta$, which we approximate as

$$\langle J'M'|\mu \cos\theta|RM\rangle \simeq \mu\,\delta_{M'M}\,\epsilon_{J'R}\,, \tag{5.18}$$

where $\epsilon_{J'R} \simeq \langle J'|R\rangle$, which for arbitrary quantum number can be calculated directly. However, we will merely estimate $\epsilon_{J'R} \sim 1$. Equation (5.18) implies that the coupling is most important for translations in the direction of the local electric field when the gradient of the field in that direction is comparable to the gradients perpendicular to that direction.

The required translational matrix elements are

$$\begin{aligned}\langle \underline{k}|z\xi_{zz}|0\rangle &= \frac{\xi_{zz}}{L^{3/2}}\sqrt[4]{\frac{\alpha^3}{\pi^3}}\int_{-\infty}^{+\infty} e^{-ik_x x-\frac{\alpha}{2}x^2}dx\int_{-\infty}^{+\infty} e^{-ik_y y-\frac{\alpha}{2}y^2}dy\int_{-\infty}^{+\infty} e^{-ik_z z-\frac{\alpha}{2}z^2}z\,dz \\ &= -\xi_{zz}\sqrt[4]{\frac{(2\pi)^6}{L^6\pi^3\alpha^7}}\,k_z\,e^{-k^2/2\alpha}\,,\end{aligned} \tag{5.19}$$

where

$$\alpha = \frac{M\omega}{\hbar}\,. \tag{5.20}$$

Therefore,

$$\begin{aligned}|H'_{1J'M',000}|^2 &= \frac{\mu^2\xi_{zz}^2}{8\alpha}\delta_{M'0}\,, \\ \left(\frac{L}{2\pi}\right)^3|H'_{\underline{k}J'M',000}|^2 &= \frac{\mu^2\xi_{zz}^2}{\pi^{3/2}\alpha^{7/2}}k_z^2\,e^{-k^2/\alpha}\,\delta_{M'0}\,,\end{aligned} \tag{5.21}$$

and we will further estimate $k_z^2 = 1/3\, k^2$ in the last term. The width is then given by

$$\gamma = \frac{\pi\sqrt{2A}}{3}\left(\frac{M}{\pi\alpha\hbar^2}\right)^{3/2}\frac{\mu^2\xi_{zz}^2}{\alpha}\left(\frac{2A}{\hbar\omega}\right)\sum_{J'}\left[J'(J'+1)\right]^{3/2} e^{-\frac{2A}{\hbar\omega}J'(J'+1)} \tag{5.22}$$

We will estimate ξ_{zz} as

$$\left|\xi_{zz}\right| = \frac{3\mu\delta}{s^4}, \tag{5.23}$$

with s as the mean separation between molecules at a given temperature, and where $\delta = |z|/s$ is a measure of the distance along the field that the molecule moves before the field changes appreciably. We will take $.1 \leq \delta \leq 1.0$. The rotational constant A for typical diatomic, polar molecules is of order 1 mev and the translational quantum $\hbar\omega$ is of order 4-5 mev.[73]

5.3 ROTATIONAL LINE SHAPE IN LIQUID HYDROGEN BROMIDE

Diatomic polar molecules, such as those of the hydrogen halides, HF, HCl, HBr, and HI are the simplest molecules which exhibit hindered rotations in the liquid state. However, the neutron spectra[124] of liquid HF and HCl indicate low energy transitions associated with motions of larger basic units than a single molecule, thus indicating polymer formation. These low energy transitions of less than .02 ev cannot be the characteristic vibrations of a single molecule as can be seen in Table I.

TABLE I

MOLECULAR CONSTANTS OF THE HYDROGEN HALIDES

	$h\omega_{vib}$(ev)	μ(D)	A(ev)	r_e(Å)	b_H(Å)	b_{hal}(Å)
HF	.492	1.91	.0026	.9166	.8708	.0458
HCl	.358	1.07	.0013	1.2747	1.2395	.0352
HBr	.319	.79	.0010	1.4140	1.4020	.0120
HI	.287	.38	.0008	1.6040	1.5960	.0080

In line with the expected decreasing strength of the hydrogen bonding association with decreasing electronegativity of the anion, the liquid HBr neutron scattering data[124] (see Fig. 8) shows less evidence of polymer formation, although assignment of two peaks was made in a later version of this work.[125] This later paper also pointed out that the broad maximum may be composed of other unresolved lines. Thus, there is some doubt that the shape of a hindered rotational line has been resolved in diatomic liquid spectra. However, we will calculate the width γ for liquid HBr using the measured spectrum as a criterion to judge the order of magnitude obtained.

For HBr we find from Table I that $\mu = .79$D and A = 1 mev, and we will use M = 80 amu. We further estimate s = 2Å, $\omega = 10^{13}$ sec^{-1}, and $\delta = 2/3$. Using the above values in Equation (5.22), we find a value of $\gamma \cong .6$ mev. This value implies a lifetime of 6×10^{-12} sec. The predicted width appears reasonable in view of the measured spectrum and the lifetime

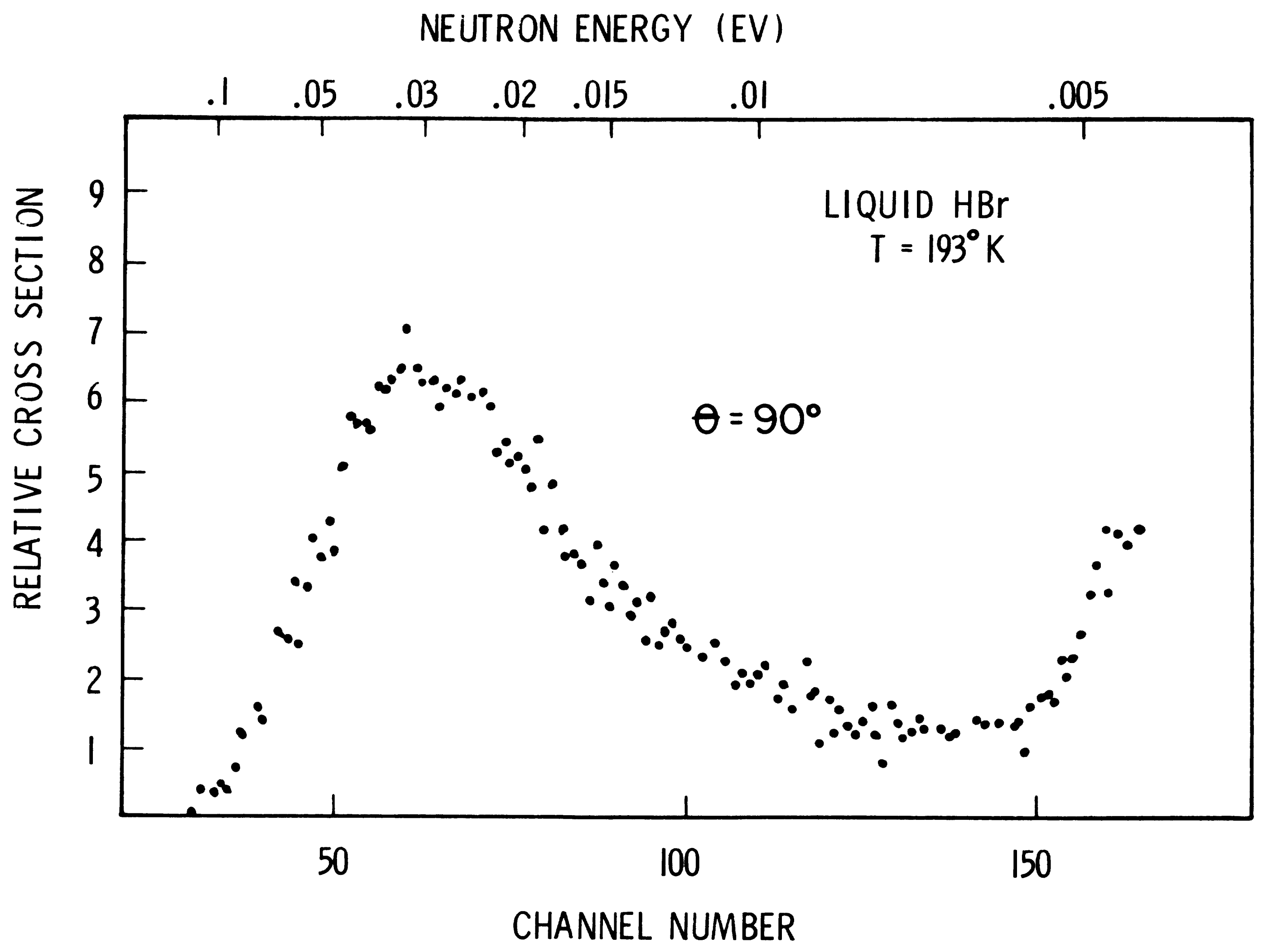


Figure 8. Relative differential scattering cross section of liquid hydrogen bromide at a scattering angle of 90°.

is of the order of magnitude found for other hydrogenous liquids.[123] Further, if Equation (5.1) is assumed to hold, and we estimate $\tau_p = h/E_{hr}$ where E_{hr} is the energy of the hindered rotation transition, then

$$E_a = k_B T \ln\left(\frac{\tau E_{hr}}{\hbar}\right).$$

For HBr, this estimates the activation energy to be .2 ev, which is of the order of hydrogen bond energies.

Thus it seems likely that this simple, intuitive model describes the dominant features of the relaxation of local order in diatomic polar liquids and yields reasonable order of magnitude estimates of the local order time. The ability to judge whether or not the shape of a hindered rotational line is determined by the lifetime of the states or the statistical fluctuations of these states awaits clarification of the experimental line shape.

CHAPTER VI

SUMMARY AND CONCLUSIONS

> "A man would do nothing if he waited until he could do it so well that no one would find fault with what he has done."
>
> Cardinal Newman

This last chapter is devoted to discussing the conclusions drawn from this investigation and some clarifying discussion in summarizing what has been accomplished here. We have concerned ourselves with molecular rotational dynamics as revealed by inelastic neutron scattering, with our primary interest being in the case when the molecules are in the liquid state.

Our motives have been twofold in pursuing such an investigation. First, such knowledge will have immediate application in the design of nuclear power plants. With reliable differential scattering cross section data for the reactor materials it becomes possible to attempt detailed calculations of the dependence of thermal neutron flux on such quantities as neutron energy, position in the reactor, and direction of neutron flow. Although the ability to calculate an actual reactor in detail is still limited by the capacity of the computers to describe the geometrical structure of the reactor, there is no possibility of correct calculations unless the relevant basic cross section information is known. Investigations of the energy transfer cross sections for reactor materials is, therefore, necessary if advantage is to be taken of the opportunity which the large computers offer for doing accurate neutronic design of reactors. Moreover, less detailed multigroup computational techniques can be improved because group constants can be calculated more reliably. Since it will never be true that experimental data will cover exactly the materials and physical conditions in every practical problem, the development of models and computational techniques capable of yielding differential scattering cross sections satisfactory for reactor physics calculations is imperative. This is particularly true for liquids.

Second, the use of neutron inelastic scattering as a tool for studying molecular dynamics of molecules whether they are in the gaseous, liquid, or solid state is finding increased applications to which it is uniquely suited. But in order to interpret correctly the complex distributions in energy of scattered neutrons, the experimentalist must have recourse to a reliable theory or model and computational technique. This study of molecular dynamics is particularly important in the liquid state where such information can be employed in finding a correct theory of liquids. Thus the results of this work would be of interest to researchers in molecular dynamics and liquid dynamics as well as to reactor physicists.

To the extent that effects like rotation-vibration interactions, rotation of the axis of vibration during scattering, and Coriolis effects can be neglected, it is appropriate to consider the dynamics of molecular translation, rotation, and vibration separately. Taking into account the present experimental facts-of-life concerning resolution and energy range, emphasis on the analysis of rotational degrees of freedom follows naturally. However, it must also be realized that experimental neutron scattering will probably never achieve the resolution of the infrared or microwave techniques, and that the large sequences of levels seen with those techniques will therefore probably never be seen in the neutron experiments. Coupled with the expense of reactors as sources of neutrons, these disadvantages can only be overcome by exploiting the special and unique advantages that neutron scattering can offer. Thus studies like the present one to see if a unique role for neutron scattering can be found in new applications are of particular pertinence to the continuing successful application of inelastic neutron scattering studies.

The study of molecular rotational dynamics for molecules as simple as CH_3OH or C_2H_6 requires a description of the internal rotational degree of freedom. Whether the internal rotation or some other aspect of the dynamics is being studied, allowance for the internal rotational effect must be made in the scattered spectra. The adoption of the semi-rigid molecule model allows a derivation of simple, rotational Hamiltonians for symmetric and some asymmetric molecules with this internal rotational degree of freedom when the internal barriers are expandable in rapidly convergent Fourier series. The limiting cases of internal torsional oscillations in threefold equal barriers and free internal rotations are described in this investigation. The demands of the neutron scattering cross section formalism used here for simple expressions for the wave functions excluded rigorous analysis for asymmetric molecules or for the intermediate case of hindered internal rotation since perturbation expansions of the wave functions require substantial numerical work to obtain cross sections. The description is believed to be applicable, however, not only to symmetric molecules but also to hydrogenous asymmetric molecules where direct scattering, which is quite sensitive to molecular dynamics, predominates over the coherent, symmetry-sensitive scattering. Now that the foundation has been laid, the extension of this description to other barrier shapes is possible. Internal barriers of the form

$$V(\alpha) = \frac{V}{2}(1 - \cos n\alpha),$$

have been discussed by Teller and Topley.[126] The form

$$V(\alpha) = \frac{V_1}{2}(1 - \cos\alpha) + \frac{V_3}{2}(1 - \cos 3\alpha),$$

which is believed to represent the barriers in ethylene dichloride and dibromide say, might be used. More complex cases such as tetramethylmethane, in which each of the four methyl groups exhibit internal rotation about the bond to the central carbon atom,[127] might also be explored.

Due to the effective coupling between internal and over-all rotation <u>as seen by the neutron</u> even in symmetric molecules, the description of over-all rotation is likewise of considerable import. Previous efforts of several investigators can then be used advantageously in describing the total rotational effect.

In the case of free over-all rotations, we are lead to rigorous expressions for the scattering cross section of symmetric molecules which portend extensive computational efforts. In lieu of approximate forms for the 3-j symbols which would speed computations, a convenient approximation of the cross section formalism was sought which would allow computations. In a restricted range of applicability, a quasi-classical approach patterned after the Krieger-Nelkin theory was attempted and a way of finding corrections was pointed out. Basically, this is an unsatisfactory way to proceed, but nonetheless an all too common one.

A means by which the over-all rotational motions of polar molecules in condensed systems are hindered was obtained previously by assigning the hindrance to purely electrostatic effects, specifically to the coupling between the dipole moment and a uniform and constant local electric field, which represents the effects of the surrounding molecules and whose magnitude is approximately the same as the crystalline field in the corresponding solid. Reinterpreting this local field as not only accounting for the orientation-dependent intermolecular force but also including the hindering effect of a weak hydrogen bond, extension of the theory to associated hydrogeneous liquids is proposed. The particular form of over-all rotational hindrance considered here affects only one angular displacement, so there will still be free over-all rotations associated with the other two over-all rotational degrees of freedom of the molecule.

Under the condition of strong coupling this description of hindered over-all rotation leads to useful wave functions for symmetric molecules. But the hindered over-all rotational energy spectrum of an asymmetric molecule should also consist of an equally-spaced set of levels, since the energies associated with hindered over-all rotation depend on system symmetries only through a level spacing $(2\lambda A)^{1/2}$, which is that of a two-dimensional isotropic oscillator. It then appears that the effects of hindered over-all rotation, as well as internal rotation, on neutron scattering by an asymmetric molecule may be approximated by using symmetric molecule wave functions. Still, although the energies may be correct in the spectrum the scattered intensity may be significantly influenced by the asymmetry.

Using the present descriptions of molecular rotation, over-all and internal, hindered and free, the differential cross sections for slow-neutron inelastic scattering are calculated. Limiting forms which are particularly simple and useful in special cases have been sought throughout. Only simplified descriptions of translational motions have been employed, namely, the free gas or independent oscillator. Vibration has been dealt with only as a zero-point motion. As a consequence of the assumption of no dynamical coupling between molecules inelastic energy transfers are possible only by direct and "inner" scatterings. Therefore, these effects determine the spectra of scattered neutrons. The elastic "outer" effect, which can be important in determining angular distributions or diffraction patterns (discussed in Appendix E), has not received any appreciable attention in this investigation due to our emphasis on rotational dynamics. However, it should be pointed out here for completeness that recent work[128] on the coherent scattering of neutrons by liquid metals has improved on the convolution approximation,[18] and the so-called Kohn anomalies[129] observed with neutrons in crystal phonon dispersion curves[130] are predicted in liquid metals as evidence of correlated motion.

By its very nature the study of "line shape" in spectra is a more detailed and refined analysis of the various factors associated with the transition which is giving rise to the line in the spectrum. A careful review of the neutron line shape formalism based on the damping theory has been presented and applied to hindered rotational lines of diatomic polar liquids using the simple model of hindering rotation employed earlier. By allowing the local order which gives rise to the hindered rotational states to "decay," thereby letting a molecule become "gas-like," a position-, orientation-dependent perturbation ascribes a width to the levels, which is a direct measure of their lifetime. An order of magnitude estimate of the average width for liquid hydrogen bromide gave a value of .6 mev, which implies a lifetime of 6×10^{-12} sec. The role which the shift of the level plays as a measure of the statistical fluctuation of the local order is pointed out, and a method for calculating the shifts which includes their temperature dependence is described on the basis of the same model. It thus appears that neutron line shape measurements will prove to be suitable microscopic probes in the study of intermolecular forces and bonds in liquids.

Entering into any such investigation are questions concerning the extent to which the single-molecule basis of the theory can be applied to physical systems. Such questions become particularly pertinent in discussing such systems as associated polar liquids, where dimers and polymers in chains and rings may be formed for short periods due to bonding between molecules. But such questions cannot currently be answered conclusively for many substances from their presently known properties. Thus the delineation of the classes of substances for which a single-molecule theory is necessary and sufficient cannot be made without further investigation. In any case, the complete single-molecule theory must be available and well understood so that deviations from expected behavior can be interpréted rightly as being due to polymer formation.

In view of the reasonable agreement obtained between the calculations presented here and the limited experimental data available, a number of scattering experiments are suggested which will subject the theory proposed in this investigation to more thorough experimental tests. First of all, many other molecules in the gaseous state have internal torsional oscillations or free internal rotations and neutron measurements have not yet been made on them. With respect to the free internal rotation cases, particularly, data at more than one angle is needed to test the angular dependence of the theory. Then, cold-neutron measurements on liquid methyl mercaptan as companions to those of Sanderson and Rainey on liquid methyl alcohol should provide a direct test of the inclusion of hydrogen bonding effects. Also, other polar molecules in the liquid state display internal torsional oscillations or free internal rotations and it may be of interest to study these with neutrons. The temperature dependence of the theory should likewise receive experimental attention, particularly the line shape aspects.

The present investigation provides a basis which can be modified and extended in subsequent work, of course, always within the framework of a model approach. The first and most important step should be calculations of the rigorous quantum results for gases, particularly in the low momentum transfer region. Coupled with any such effort however, should be a more careful treatment of the averaging of vibrations, since McMurry[131] has shown that an "exact averaging" procedure produces significant differences in some cases. Inclusion of inelastic vibrational transitions and rotation-vibration interactions should be made for completeness. Besides the extension to other barrier shapes already mentioned, it may be of interest to see how involved the treatment of the intermediate case of hindered internal rotation may be. The closely related problem of hindered rotations of ions at lattice sites in crystalline solids, such as various ammonium halides and other ammonium salts, is of considerable interest, although there three rotational degrees of freedom are hindered and consideration of higher multipole couplings such as octapole-octapole is necessary due to the symmetry of the ion groups and crystal lattices.

This investigation has attempted to explore a possibly unique role for inelastic neutron scattering in the analysis of rotational dynamics of molecules in gases and liquids. For such a study a "model" approach as adopted here is appropriate, and leads to useful information on molecular motions. The philosophy of this model approach has been guided by the goal of interpreting experimental data. It is the role of more general, basic and systematic approaches to explore the unmeasured systems and to provide a theoretical basis for the development of models.

To place a final comment in perspective, let us quote P. A. Egelstaff in his remarks[132] summarizing the most recent international symposium on inelastic neutron scattering:

> "In the case of experiments where many peaks are seen in the data we hear phrases such as hindered translation, torsional oscillations, libration, free rotation, hindered rotation, and so on. These phrases are vague, because if you want a complete and proper statement you must turn these phrases into a theory which enables you to discuss the energy of the levels, the relative magnitude of the different peaks, the absolute magnitude of the peaks, the shape of the line, and whether the lines are single states or multiple states, etc...Theoreticians will have to calculate the things I listed above before we can talk adequately about these processes."

It is hoped the theory presented in this dissertation will allow an adequate discussion to begin.

APPENDIX A

SOME PROPERTIES OF NEUTRONS

The neutron was first observed experimentally in 1932 by Curie - Joliot, and by Chadwick, who is credited with the "discovery" of the "neutron." The name "neutron" was actually bestowed some 12 years earlier by Rutherford.

Its mass is: $M_n = 1.008982 \pm .000003$ amu

It has no detectable net electric charge.

It is a Fermion of spin 1/2 $\hbar$.

It has a magnetic dipole moment of -1.913 nuclear magnetons (1 nuclear magneton = $e\hbar/2M_pc$).

Free neutrons are radioactive with a half-life of 12.8 minutes and will "fall" in a gravitational field. The beta-decay of free neutrons is given by:

$$_0n^1 \longrightarrow {_1p^1} + {_{-1}e^0} + \nu ,$$

where ν is a neutrino.

High-energy electron-neutron scattering experiments which measure the second moment of the charge distribution within a neutron, suggest that the neutron is a core of positive charge, surrounded by a region of negative charge, with finally, a shell of positive charge.[133] The latest measurements of neutron form factors indicate they are extremely small or zero.[134]

Slow-neutron inelastic scattering compares advantageously with other methods of probing matter for the following reasons. The neutron scattering length is constant within a factor of 2 or 3 for nearly all atoms, whereas X-ray scattering amplitudes have a linear dependence on the atomic number of the scatterer. Slow-neutron scattering lengths are independent of the angle of scattering but both X-ray and electron scattering amplitudes fall off with increasing angle of scatter due to the atomic form factor. Compared to the energy of the scattered X-ray or electron, the energy transfers associated with the scattering process are negligible for X-ray and electron diffraction, so that these methods, although quite sensitive to target symmetry, provide no information on the atomic motions. A detailed comparison of electromagnetic and neutron scattering studies of solids has been given by Blume.[135] He points out that considerable information about atomic motions can be obtained with neutrons that cannot be obtained with X-ray or light scattering simply due to the energy-wavelength "kinematical" differences (for neutrons, $\lambda = h/\sqrt{2mE}$, while for photons, $\lambda_p = hc/E$).

APPENDIX B

STATISTICAL THERMODYNAMICS

In this appendix we wish to summarize briefly the elements of statistical thermodynamics[136] used in this investigation and to point out the relationship between the fields of slow-neutron inelastic scattering and kinetic theory. Considerations of kinetic theory, thermodynamics and/or statistical mechanics, enter the description of the neutron differential scattering cross section through the initial state average, $\sum_i P_i \langle i | \quad | i \rangle$. More specifically P_i , the probability of initial state occupation, is inversely proportional to the characteristic function of statistical mechanics which is called the partition function (so named by Darwin and Fowler), state sum, or zustandsumme (as called by Planck).

In the next appendix we will discuss the history of some "theories of liquids." These equilibrium theories are concerned almost exclusively with the calculation of the partition function of a liquid with the use of statistical mechanical concepts, and the subsequent use of the partition function in the calculation of thermodynamic quantities.

In essence, the three related disciplines of thermodynamics, statistical mechanics, and kinetic theory were founded with Joule's demonstration that motion and heat are equivalent, because this mechanical theory of heat is a major consideration of each discipline. Without attempting to define the subject matter of each discipline, we wish to extract a broad area with which each deals. We will describe kinetic theory broadly as including nearly all studies of molecular motion and its effects. Thermodynamics postulates the first and second laws of thermodynamics and derives simple, general, and fundamental results for such quantities as entropy, enthalpy, heat capacity, and equations of state (i.e., equations expressing a relation between the pressure, volume, and temperature of a system). Statistical mechanics is a detailed discipline, undertaking to answer the questions, how is each atom or molecule of the substance moving, on the average, and how do these motions lead to observable phenomena. Clearly, a detailed study of the nature of matter necessitates a knowledge of all three disciplines.

Once the partition function of statistical mechanics is known as a function of the independent variables of an ensemble of systems, all the thermodynamic properties of the system can be derived due to the so-called Gibbs relations which relate thermodynamic quantities to the partition function. The partition functions of both the canonical ensemble (representing closed, isothermal systems) and the grand canonical ensemble (representing open, isothermal systems) have been employed in the theory of liquids.[137,138] The canonical ensemble partition function Z is defined as the sum over all states i of the Boltzmann factor:

$$Z \equiv \sum_i e^{-E_i/k_B T}.$$

Then the Gibb's relation for the Helmholtz free energy is

$$A = -k_B T \ln Z$$

Similarly, the Gibb's free energy is

$$G = -k_B T \ln Z + V k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T ,$$

and so on.

APPENDIX C

A MEAGRE HISTORY OF SOME THEORIES OF LIQUIDS

About 400 B.C. the Greek philosophers Leucippus, Democritus, and their pupils pictured a world made out of minute particles or atoms which were in constant motion. In 95 B.C. Lucretius,[139] who was familiar with the earlier writings, pictured gases somewhat as they are pictured today. However true these philosophic speculations seem today, they were then no more than wild guesses. Much later, but also to be classed among the philosophic speculations, is Bernoulli's 1738 publication "Hydrodynamics" because at that time there was no experimental basis for his assumptions.

It remained until the middle 1800's when the famous experiments of Rumford and Joule on the relation between heat and work were in progress, to bring forth the papers, based on an experimental footing, of Kronig (1856) and R. Clausius (1857) which stimulated Kelvin, Maxwell, Boltzmann and others between 1860 and 1890 to further develop the kinetic theory. But because no proof of the separate existence of the atoms and molecules had been obtained, nor had any observations been made that could really demonstrate the continual thermal motions of the molecules, the theory remained no more than an hypothesis.[140]

Jean Perrin[141] in 1908 succeeded in quantitatively demonstrating the existence of the continual thermal motions of the molecules of a liquid by a study of the Brownian movements of suspended particles and thereby established the kinetic theory.[140]

In 1878 liquids were first characterized by van der Waal's view that there is an analogy between a liquid and a gas, the liquid being only more highly compressed. As there is no absolute discontinuity separating these two states of matter, this is formally correct. That is, conditions of temperature and pressure can be so regulated that the transition from gas to liquid is continuous above the critical point. In van der Waal's theoretical equation-of-state of an imperfect gas, which he obtained by largely intuitive reasoning but which gives a qualitatively, roughly correct picture of thermodynamic properties, the total volume V is replaced by an effective free volume, $V_f = V - Nb$, where N is the number of molecules of radius b and the assumption is that $Nb \ll V$. However, in liquids, the free volume is very much smaller than the total volume (taken as the volume of liquid not the volume of the container), the molecules taking up most of the space. This is an important practical difference. But it wasn't until the 1930's that this practical difference was recognized.

At about the same time certain other facts about liquids were found, such as: (a) a general 10 per cent increase in volume upon melting a solid, (b) a similarity of specific heats of solids and liquids near the melting point, and (c) the existence of local order as found by X-ray diffraction and later confirmed by neutron diffraction. These facts lead to the reapproximation of the liquid by the crystalline solid state. At this point two hypotheses were formulated: (a) the micro-crystalline hypothesis, and (b) the quasi-crystalline hypothesis. A large number of different models and theories ascribing to the liquid various degrees of "crystallinity" and "lattice-like" character all assumed the quasi-crystalline hypothesis, the micro-crystalline hypothesis in which clusters of atoms move as a group never being completely developed by any author. The recent trend in the theory of liquids began in the 1940's with the development of molecular distribution function theories.

At the present time theories of the liquid state of matter fall into two broad classes. Lattice theories[142] start from a description of the structure, usually a simplified and approximate description, and leave the question of how the structure is determined by the molecular properties to be answered after the fact. Distribution function theories,[143] so called because their formulations of the problem involve distribution functions which specify the probability of finding sets of molecules in particular configurations, are concerned with the process by which the intermolecular forces determine the structure, since a correct description of this process should lead, in principle, to a correct description of the actual structure.

Further classification of lattice theories, into cell theories, hole theories, and tunnel theories, as well as direct computation methods, is possible. Related to the cell theories, but requiring digital computers, the direct computation Monte Carlo method of ensemble averaging and the molecular dynamics method of time averaging, while furnishing some valuable information, do not offer satisfying theories of the liquid.

The cell theories start from the assumptions: (1) that the available volume can be divided into identical cells, one for each molecule, and that only configurations in which every cell contains one molecule need to be considered; (2) that the cells can be chosen so that their centers form a regular lattice; and (3) that the molecules can be regarded as moving independently in their cells. The cell theory in the form due to Lennard-Jones and Devonshire[144] (LJD) with its "smearing approximation" is essentially a theory of solids, as they indicated in later papers[145] and as was recently underlined by Barker.[142] Attempts to base the cell theories on a variation principle and to use the variation principle to improve the cell theories have led to unsatisfactory results.[142] The justification for the cell theory approach lies in the fact that correlation effects, neglected by assumption (3) above, are small, and the best way to improve the cell theories is to allow for the correlation and "communal" effects. However, while the correlation effects can be taken into account to improve cell theories, the intractable nature of the problem of evaluating the communal effect for simple liquids limits the prospects for cell theories completely describing "liquids in general." Essentially similar difficulties occur in the elegant cell cluster theory of de Boer.[146]

The hole theories start from the assumptions: (1) that the available volume can be divided into identical cells, the number of cells, exceeding the number of molecules; (2) that the cells can be chosen sufficiently small that configurations with more than one molecule in any cell can be neglected entirely; (3) that the cells can be chosen so that their centers form a regular lattice; and (4) that the molecules can be regarded as moving independently in their cells. The hole theories, which were proposed as an improvement over cell theories and do account for the communal entropy give rather doubtful gains which are more than offset by the increased complexity of the theory, with the possible exception of the semi-empirical order-disorder theory of melting. A variational hole theory has also been proposed, but it is not superior to the simpler approach,[142] and the improvements to be expected from the cell cluster theory with holes is not large if one can judge on the basis of the simpler theories.

It should be mentioned here that the significant structure theory of liquids[146] is probably considered a semi-empirical theory. It is, however, the most accurate in predicting thermodynamic properties and has had considerable success with transport parameters.

The tunnel theories[142] are new, having been first discussed in 1960. They begin with the assumptions: (1) that the molecules move in lines down "tunnels" whose walls are formed by neighboring lines; (2) that the line centers form a regular close-packed lattice; (3) that the molecules in a given tunnel move independently of those in other tunnels; and (4) that the longitudinal and transverse motions in a tunnel are separable. Better agreement with the thermodynamic data and radial distribution function data for liquid argon have been achieved with the tunnel theory than any of the above theories.

Ookawa[113] in 1960 proposed a micro-crystalline model with the following features: (1) a liquid is pictured as a crystalline solid threaded by a lattice of dislocations, (2) the spacing of the dislocation lattice is assumed to be of the order of a few atoms, (3) the elastic distortion of the lattice in bulk rather than a local distortion at the core of the constituent dislocations is assumed, (4) the anharmonicity of the potential is accounted for by the assumption of a modulation-of-eigenfrequency relation for the transversal shear waves, the cause of modulation being the shear strain of the material in a state of self-strain, (5) transverse thermal shear waves of wavelength longer than a critical wavelength are assumed to degenerate into translational motion, (6) it is a one-parameter model, this parameter being the modulation coefficient, and (7) the Hamiltonian reduces to a sum of gas and oscillator Hamiltonians. Ookawa calculated the partition function and demonstrated a kind of first-order phase transition, but made no comparison with other theories or thermodynamic data.

The only explicit results available from distribution function theories are derived from the integral equations of Kirkwood[147] and Born and Green,[148] which are based on the "superposition approximation" expressing the triplet distribution function in terms of the pair distribution function. Agreement of results for rigid spherical molecules compared to Monte Carlo calculations is unsatisfactory at high densities.[149] In any case, the pair distribution function does not describe the structure in detail, since many different three-dimensional structures may correspond to the same radial distribution function. Thus it seems that any theory which attempts to describe liquids in terms of pair and perhaps triplet distribution functions is faced with a fundamental difficulty. However, this is the only systematic approach and may well lead to a satisfactory theory. A very interesting approach is that of Kadanoff and Martin.[150]

In the next appendix we point out several models employed in describing liquids in neutron scattering studies.

APPENDIX D

SIMPLE LIQUID--MODEL CALCULATIONS

In this appendix we summarize the results of calculations we have carried out using some highly simplified models of the center-of-mass translations of the molecules of a liquid. We briefly discuss three models and point out where additional models have been proposed for interpreting neutron scattering studies of liquid dynamics.

Two extreme models are frequently employed and really represent the limiting models of the gaseous and solid states rather than liquids *per se*. These are the ideal gas model and the harmonic oscillator or Einstein crystal model.

The ideal gas model corresponds to van der Waal's view that a liquid is simply a gas only more highly compressed. This clearly is an over-simplification since it is well known that each molecule in a liquid has many molecules with which it is interacting, in contrast to a dilute gas where the mean free path between binary collisions is a meaningful concept.

The harmonic oscillator model is the dynamical formulation which logically accompanies the quasi-crystalline cell model of Lennard-Jones and Devonshire,[144] which was proposed in an attempt to take into account the molecular interactions neglected in the ideal gas model. (However, the cell model allows anharmonic vibrations.) It is the opposite extreme from the ideal gas model in that the translational motion of a molecule is assumed to be completely hindered except for the oscillations within the harmonic potential created by its neighbors.

It further maintains the long-range ordering which is characteristic of the solid not the liquid state.

When the ideal gas model Hamiltonian,

$$H_g = \sum_l \frac{p_l^2}{2M}, \tag{D.1}$$

is employed in the expression,

$$\langle \chi_{ll} \rangle_T = \sum_i P_i \langle i | e^{i\frac{t}{\hbar}H_g} e^{i\underline{\kappa}\cdot\underline{R}_l} e^{-i\frac{t}{\hbar}H_g} e^{-i\underline{\kappa}\cdot\underline{R}_l} | i \rangle, \tag{D.2}$$

with the fact that

$$e^{i\underline{\kappa}\cdot\underline{R}} f(\underline{p}) e^{-i\underline{\kappa}\cdot\underline{R}} = f(\underline{p}-\hbar\underline{\kappa}), \tag{D.3}$$

the direct scattering thermal average which results is

$$\langle \chi_{ll} \rangle_T = \sum_i P_i e^{-i\frac{t}{\hbar}E_R} \langle i | e^{i\frac{t}{\hbar}\underline{\kappa}\cdot\underline{p}_l} | i \rangle, \tag{D.4}$$

where the recoil energy is

$$E_R = \frac{\hbar^2\kappa^2}{2M}. \tag{D.5}$$

Since the energy states form a continuum $\left(|i\rangle = N_k e^{i\underline{k}\cdot\underline{r}}\right)$ we replace the sum over i by an integral over k, where P_i is clearly the Boltzmann distribution in momentum space $(\underline{p}=\hbar\underline{k})$, so that

$$\langle \chi_{ll} \rangle_T = \frac{\hbar^3}{(2\pi M k_B T)^{3/2}} e^{-i\frac{t}{\hbar}E_R} \int d^3k \, e^{-\frac{\hbar^2 k^2}{2Mk_BT}} e^{i\frac{t}{\hbar}\frac{\hbar^2\underline{\kappa}\cdot\underline{k}}{M}}. \tag{D.6}$$

By completing the square in the exponent of the integrand and doing the trivial momentum integration, we obtain

$$\langle \chi_{ll_T} \rangle = e^{-i\frac{t}{\hbar}E_R} e^{-\frac{k_B T E_R t^2}{\hbar^2}}. \tag{D.7}$$

To compute the direct scattering cross section from the formula

$$\frac{d^2\sigma_d}{d\Omega dE_f} = a_{inc}^2\sqrt{\frac{E_f}{E_i}}\,\frac{1}{2\pi\hbar}\int dt\, e^{-i\epsilon_n \frac{t}{\hbar}}\,\frac{1}{N}\sum_{\ell} \langle \chi_{\ell\ell}\rangle_T, \qquad \text{(D.8)}$$

we must complete the square on t in the exponent of the integrand, and perform the time integration, obtaining the desired result:

$$\frac{d^2\sigma_d}{d\Omega dE_f} = a_{inc}^2\sqrt{\frac{E_f}{\pi E_i \mathcal{E}^2}}\; e^{-\frac{(\epsilon_n+E_R)^2}{\mathcal{E}^2}}, \qquad \text{(D.9)}$$

where

$$\mathcal{E}^2 = 4E_R k_B T. \qquad \text{(D.10)}$$

The interference scattering cross section in this model is often approximated simply as

$$\frac{d^2\sigma_i'}{d\Omega dE_f} = a_c^2\,\frac{\rho_\infty}{N}\int d^3r\, e^{i\underline{\kappa}\cdot\underline{r}}\, g(r)\,\delta(E_i-E_f), \qquad \text{(D.11)}$$

where ρ_∞ is the average density and $g(r)$ is the radial distribution function of a gas.

Now use of the harmonic oscillator model Hamiltonian,

$$H_S = \sum_{\ell}\left[\frac{p_\ell^2}{2M} + \frac{1}{2}M\omega^2 r_\ell^2\right], \qquad \text{(D.12)}$$

where ω is the oscillator frequency and $\underline{r}_\ell = \underline{R}_\ell + \underline{u}_\ell$ with $\underline{R}_\ell$ as the equilibrium position vector and $\underline{u}_\ell$ as the displacement from equilibrium, in the direct scattering thermal average

$$\langle \chi_{\ell\ell}\rangle_T = \sum_i P_i \langle i|\, e^{i\underline{\kappa}\cdot\underline{u}_\ell(t)}\, e^{-i\underline{\kappa}\cdot\underline{u}_\ell}\,|i\rangle, \qquad \text{(D.13)}$$

where the Heisenberg time-dependent operator is,

$$\underline{u}_\ell(t) = e^{i\frac{t}{\hbar}H_s}\,\underline{u}_\ell\,e^{-i\frac{t}{\hbar}H_s}, \tag{D.14}$$

yields

$$\langle \chi_{\ell\ell}\rangle_T = \sum_i P_i\, e^{\frac{\kappa^2}{2}[\underline{u}_\ell(t),\underline{u}_\ell]}\langle i|e^{-i\underline{\kappa}\cdot[\underline{u}_\ell(t)-\underline{u}_\ell]}|i\rangle, \tag{D.15}$$

which becomes

$$\langle \chi_{\ell\ell}\rangle_T = e^{-\frac{\kappa^2}{2}\left[\langle u_\ell^2(t)\rangle_T + \langle u_\ell^2\rangle_T - 2\langle \underline{u}_\ell(t)\cdot\underline{u}_\ell\rangle_T\right]}, \tag{D.16}$$

when Block's theorem (appropriate for an oscillator coordinate Q)

$$\langle e^Q\rangle_T = e^{\frac{1}{2}\langle Q^2\rangle_T}, \tag{D.17}$$

is employed. The thermal averages of the displacements are

$$\begin{aligned}\langle u_\ell^2(t)\rangle_T = \langle u_\ell^2\rangle_T &= \frac{\hbar}{2M\omega}\,\frac{1+e^{\nu}}{1-e^{\nu}},\\ \langle \underline{u}_\ell(t)\cdot\underline{u}_\ell\rangle_T &= \frac{\hbar}{2M\omega}\left(\frac{e^{\nu}}{1-e^{-2\nu}}\right)\left\{e^{\nu}e^{-i\omega t} + e^{-\nu}e^{i\omega t}\right\},\end{aligned} \tag{D.18}$$

which gives a thermal average

$$\langle \chi_{\ell\ell}\rangle_T = e^{-D\kappa^2}\sum_{n=-\infty}^{+\infty} e^{n\nu} I_n(P\kappa^2)\, e^{-in\omega t}, \tag{D.19}$$

and hence a direct scattering cross section of

$$\frac{d^2\sigma_d}{d\Omega\, dE_f} = a_{inc}^2 \sum_{n=-\infty}^{+\infty}\sqrt{\frac{E_f}{E_i}}\, e^{-D\kappa^2} e^{n\nu} I_n(P\kappa^2)\,\delta(E_i - E_f - n\hbar\omega), \tag{D.20}$$

where

$$D = \frac{\hbar}{2M\omega}\coth\nu, \qquad \nu = \frac{\hbar\omega}{2k_B T}. \tag{D.21}$$
$$P = \frac{\hbar}{2M\omega}\operatorname{csch}\nu,$$

Consideration of the interference thermal average leads to a cross section given by

$$\frac{d^2\sigma_i}{d\Omega dE_f} = \frac{a_c^2}{N}\sum_{\ell\ell'}{}' e^{-D\kappa^2} e^{i\underline{\kappa}\cdot(\underline{R}_\ell - \underline{R}_{\ell'})}\delta(E_i - E_f), \tag{D.22}$$

which leads, in the n → ∞ limit to the familiar Bragg conditions characteristic of a solid.

We turn now to the description of the crystalline dislocation model proposed by Ookawa[113] in 1960 (see Appendix C). Its adoption as a dynamic model of molecular motion was suggested by Rosenbaum,[114] although its physical implications have not been fully explored. Basically it predicts that on the average a neutron will find a molecule of the liquid bound in a diffusing crystallite of a certain size but undergoing vibrations in the small, moving crystal lattice. In this micro-crystalline model, thermal agitation is represented by a superposition of longitudinal waves plus shear waves that lead, depending on their wavelength to either translational or vibrational modes. The model pictures a liquid as a solid threaded by a dislocation lattice such that transverse waves of wavelength longer than the lattice spacing, α , give rise to translations of the material in bulk. The Hamiltonian for an imperfect crystal of N particles of mass M is given by

$$H=\sum_{j=1}^{3N}\frac{p_j^2}{2M}+V(\underline{q}_1,\underline{q}_2,\dots,\underline{q}_N), \tag{D.23}$$

where $\underline{q}$ and $\underline{p}$ denote nuclear coordinates and moments respectively, and where making use of the harmonic approximation allows the expansion of the Hamiltonian into normal modes. Consequently,

$$H=\mathcal{U}_0+\sum_{l=1}^{3N}\left(\frac{M}{2}\dot{Q}_l^2+\frac{1}{2}\omega_l^2Q_l^2\right), \tag{D.24}$$

where $\mathcal{U}_0$ is the configurational excess energy (excess over ideal gas) and the $\underline{Q}$'s are normal coordinates. Further, resolving (D.24) into longitudinal and transversal modes yields

$$H=\mathcal{U}_0+\sum_{k=1}^{N}\frac{1}{2M}\left(C_k^2+M\omega_{1k}^2A_k^2\right)+\sum_{k=1}^{N}\sum_{i=1}^{2}\frac{1}{2M}\left(D_{ki}^2+M\omega_{2ki}'^2B_{ki}^2\right), \tag{D.25}$$

where C_k and D_{ki} are the longitudinal and transversal normal momenta respectively, and A_k and B_{ki} their corresponding normal coordinates. Now, allowing the transversal modes with $k \leqslant k_c$ to degenerate into translations we obtain as the final form

$$\begin{aligned}H={}&\mathcal{U}_0+\sum_{\nu=1}^{N/\alpha^3}\sum_{i=1}^{2}\frac{p_{\nu i}^2}{2M\alpha^3}\\&+\sum_{k=1}^{N}\frac{1}{2M}\left(C_k^2+M\omega_{1k}^2A_k^2\right)\\&+\sum_{k>k_c}\sum_{i=1}^{2}\frac{1}{2M}\left(D_{ki}^2+M\omega_{2ki}'^2B_{ki}^2\right).\end{aligned} \tag{D.26}$$

Rosenbaum[114] subsequently obtains the following incoherent scattering function by using (D.26) in the Wigner representation formalism:

$$S_{inc}(\underline{\kappa}, \omega) = \frac{1}{2\pi}\int dt\, e^{-i\omega t} e^{\frac{\beta}{2}\hbar\omega} e^{-\kappa^2\Omega(t)} , \tag{D.27}$$

where $\Omega(t)$ is approximately given by

$$\Omega(t) = \frac{\beta}{8M\alpha^3\hbar^2} + \frac{k_B T}{M\hbar^4\omega_D^4}\left[\left(1+\frac{1}{\alpha^3}\right) + 2e^{\gamma/\alpha^2}\left(1-\frac{1}{\alpha}\right)\right] + \frac{t^2}{2\hbar^4 M\alpha^3\beta}$$
$$- \frac{\left(1-\frac{1}{\alpha^3}\right)\sin\omega_D t}{M\hbar^4\omega_D^3\beta t} - \frac{2e^{3\gamma/2\alpha^2}}{\beta M\hbar^4\omega_D^3 t}\left[\sin\left(\omega_D t e^{-\gamma/2\alpha^2}\right) - \sin\left(\frac{\omega_D t}{\alpha} e^{-\gamma/2\alpha^2}\right)\right], \tag{D.28}$$

where

$$\beta = 1/k_B T ,$$
$$\kappa^2 = \frac{2m}{\hbar^2}\left[E_f + E_i - 2\cos\theta_s\sqrt{E_f E_i}\right], \tag{D.29}$$

W_D = the Debye cutoff frequency,

and γ is a modulation-of-eigenfrequencies constant such that

$$\omega'_{2ki} = \omega_{2ki}\, e^{-\gamma/2\alpha^2} . \tag{D.30}$$

Therefore, the incoherent scattering cross section is

$$\frac{d^2\sigma_{inc}}{d\Omega\, dE_f} = \frac{a_{inc}^2}{2\pi\hbar}\sqrt{\frac{E_f}{E_i}}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t} e^{\frac{\beta}{2}\hbar\omega} e^{-\kappa^2\Omega(t)} \tag{D.31}$$

where $\Omega(t)$ is given by (D.28). We may use this as our final expression for the cross section or we may attempt to approximately perform the Fourier transformation by an expansion technique (see Rosenbaum[114] for details):

$$\frac{d^2\sigma_{inc}}{d\Omega dE_f} = \frac{a_{inc}^2}{\hbar\sqrt{2\pi}}\sqrt{\frac{E_f}{E_i}}\, e^{-\hbar^2\kappa^2\left[\eta(0)+\frac{\beta}{8M\alpha^3}\right]} \sum_{n=0}^{\infty} \frac{\left[\hbar^2\kappa^2\eta(0)\right]^n}{n!}$$

$$(x)\ \frac{e^{-\frac{\hbar^2\omega^2}{D_n}}}{\sqrt{D_n}} \sum_{j=0}^{\infty} C_j^{(n)}(-1)^j H_j\left(\frac{\hbar\omega}{\sqrt{D_n}}\right), \tag{D.32}$$

where by definition

$$C_j^{(n)} = (-1)^j \frac{1}{j!}\frac{d^j}{d\tau^j} e^{\left[n\sum\limits_{\ell=3}^{\infty}\frac{\lambda_\ell}{\ell!}\left(-\frac{i\tau}{\sqrt{D_n}}\right)^\ell\right]}\Bigg|_{\tau=0},$$

$$\lambda_\ell = (-i)^\ell \frac{d^\ell}{d\tau^\ell} \ln\left[\frac{\eta(\tau)}{\eta(0)}\right]\Bigg|_{\tau=0},$$

$$\eta(\tau) = \frac{1}{2M\hbar}\Bigg[\frac{1}{(\omega_D\alpha)^3}\int_0^{\omega_D}\omega\,\mathrm{csch}\left(\frac{\beta\hbar\omega}{2}\right)\cos(\hbar\tau\omega)\,d\omega \tag{D.33}$$

$$+\frac{2e^{\gamma/2\alpha^2}}{\omega_D^3}\int_{\omega_D/\alpha}^{\omega_D}\omega\,\mathrm{csch}\left(\frac{\beta\hbar\omega}{2}e^{-\gamma/2\alpha^2}\right)\cos\left(\hbar\omega\tau e^{-\gamma/2\alpha^2}\right)d\omega,$$

$$D_n = n\lambda_2 + 2Q,$$

$$2Q = \frac{\hbar^2\kappa^2}{M\beta\alpha^3},$$

and where

$$H_j(y) = (-1)^j e^{y^2}\frac{d^j}{dy^j}e^{-y^2}, \tag{D.34}$$

are the Hermite polynomials. We have derived some further results, which are

$$C_j^{(n)} = \begin{cases} 0 & (j \text{ odd}) \\ 1 & (j = 0) \\ 0 & (j = 2) \\ \dfrac{(-1)^{j/2} n \lambda_j}{j!\, D_n^{j/2}} & (j \text{ even} > 2) \end{cases}$$

$$\lambda_j = \begin{cases} 0 & (j \text{ odd}) \\ 0 & (j = 0) \\ \hbar^2 \omega_D^2 / \alpha^3 f & (j = 2) \\ \dfrac{\hbar^4 \omega_D^4}{f}\left[\dfrac{1}{5\alpha^3} - \dfrac{1}{f\alpha^6} + \dfrac{2}{5} e^{3\gamma/2\alpha^2}\left(1 - \dfrac{1}{\alpha^5}\right)\right] & (j = 4) \end{cases} \tag{D.35}$$

$$\eta(0) \cong f/(M\beta\hbar^2\omega_D^2),$$

where

$$f = \frac{1}{\alpha^3} + 2e^{\gamma/\alpha^2}\left(1 - \frac{1}{\alpha}\right). \tag{D.36}$$

If we truncate the sum over j after 6 terms, (D.32) becomes

$$\frac{d^2\sigma_{inc}}{d\Omega dE_f} = \frac{a_{inc}^2}{\hbar\sqrt{2\pi}} \sqrt{\frac{E_f}{E_i}}\, e^{-\hbar^2\kappa^2\left[\eta(0) + \frac{\beta}{8M\alpha^3}\right]} \sum_{n=0}^{\infty} A_n, \tag{D.37}$$

where

$$A_n = (D_n^2 + n\Lambda H')\, \frac{e^{-\frac{\hbar^2\omega^2}{D_n}} \left[\hbar^2\kappa^2\eta(0)\right]^n}{n!\, D_n^2 \sqrt{D_n}},$$

$$\Lambda = 2\lambda_4/3,$$

$$H' = \frac{\hbar^4\omega^4}{D_n^2} - 3\frac{\hbar^2\omega^2}{D_n} + .75. \tag{D.38}$$

Hence, (D.37) is the desired expansion. However, A_n is greater than A_{n+1} only when the energy transfer is small or n is large. This effectively limits the useful range of (D.37) to energy transfers less than about 30 mev (judgment based on a convergence test code and reasonable time criteria).

In Fig. 9, we show a comparison of differential scattering cross sections based on free gas and Einstein crystal models for an experimental resolution of 10%. The constants employed were for liquid argon at 84°K, incident energy of 55 mev, and a scattering angle of 70°. No measurable difference is seen. However, the models predict quite different results when the resolution is 3%, as can be seen in Fig. 10. The "structure" of the oscillator model apparent at 3% is unresolved at 10% resolution. However, 10% resolution is sufficient if E_i is reduced to the cold neutron value of 5 mev. Calculations with the crystalline dislocation model show results intermediate to the above models. That is, the "structure" of the oscillator model at 3% resolution is not as pronounced but still can be seen.

The increase in the width function (D.28) without limit as time increases is in sharp contrast to the width for a solid, which becomes asymptotic to the Debye-Waller factor. This indicates that in this crystalline dislocation model a molecule is not always confined to a well localized vicinity. However, the asymptotic increase of the width with time is parabolic according to this model while it is linear for diffusive type motion.

In addition to these models, several others have been employed in describing neutron scattering studies of liquid dynamics. A simple diffusion model[18] has been proposed, and a correction to it discussed.[151]

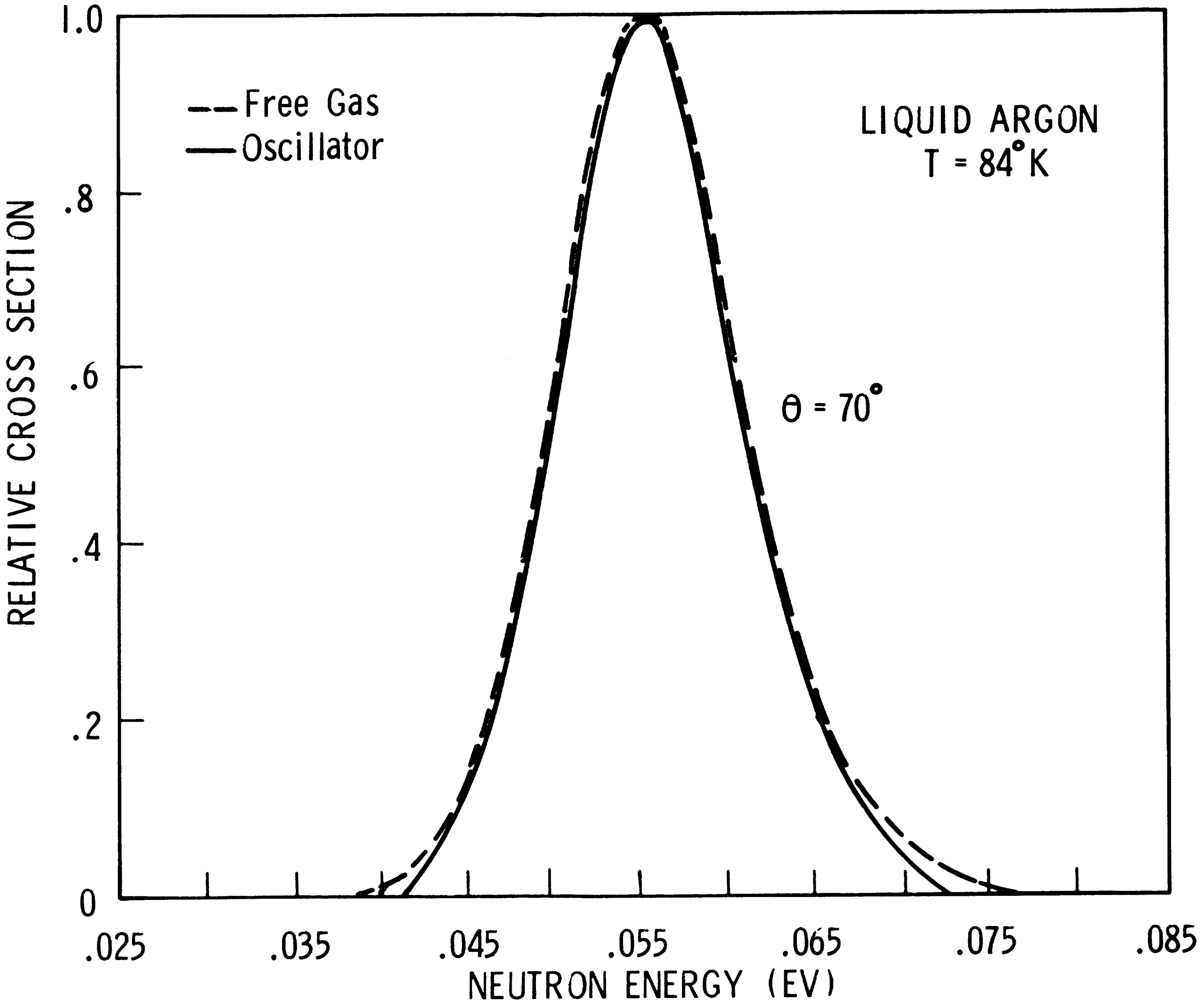


Figure 9. Comparison of free gas and oscillator models in predicting the relative differential scattering cross section of liquid argon for 10% "experimental" resolution.

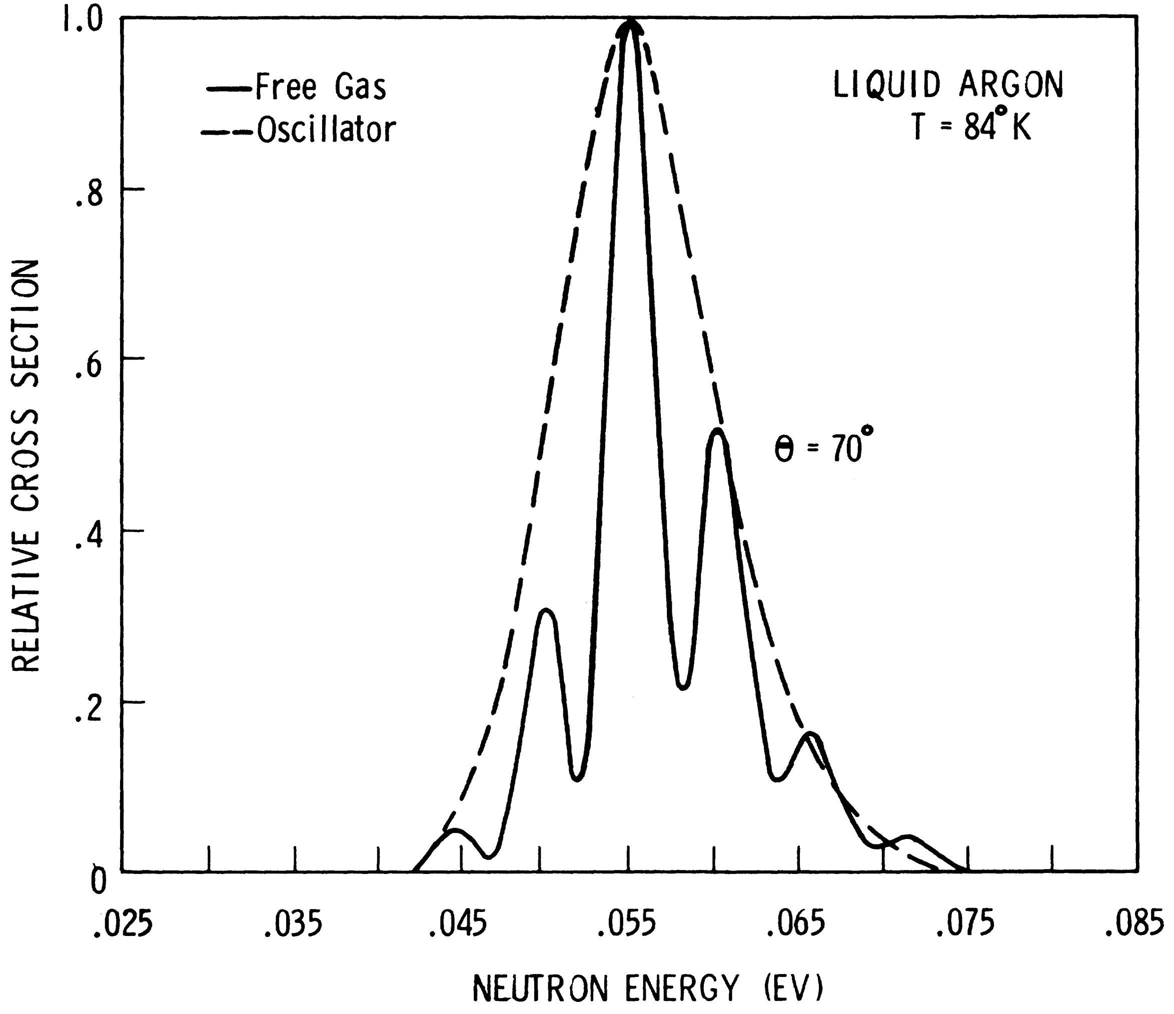


Figure 10. Comparison of free gas and oscillator models in predicting the relative differential scattering cross section of liquid argon for 3% "experimental" resolution.

Both a jump diffusion model[152] and a modification[153] of jump diffusion have been described. Schofield[154,155] has given attention to a globule model. A stochastic description has been given[115] and the Langevin equation of Brownian motion employed.[156]

APPENDIX E

NEUTRON ANGULAR DISTRIBUTIONS

One of the four classes of experimental evidence on the liquid state involves the measurement of X-ray and neutron angular distributions and their subsequent reduction to a radial distribution function. This provides information on the structure of simple liquids and liquid metals. This appendix contains a brief review of the type of information obtainable, a derivation of a relation for neutron angular distributions appropriate to a "micro-crystalline" model of liquids, and the results of calculations using this relation in comparison with other models and experimental evidence for some simple liquids.

That structural information about the arrangement of molecules in the liquid state can be obtained from X-ray diffraction (and consequently neutron diffraction), has been known since Debye[157] and Ehrenfest[158] in 1915 showed that the periodicity of a crystal structure is not required for the production of diffraction effects. Early experimental X-ray diffraction studies were carried out by Debye and Scherrer[159] in 1916 on benzene and by Keesom and De Smedt[160] in 1923 on liquid argon. In 1927, Debye[161] introduced the concept of a probability function for the distribution of intermolecular distances, and the relation of this function to the X-ray diffraction pattern or angular distribution was discussed by Zernike and Prins.[15] Debye and Menke[162] made the first quantitative application of Fourier analysis to liquid data when they measured the X-ray angular distribution of liquid mercury in 1930. The results of X-ray diffraction measurements on liquids were summarized in reviews by Gingrich[163] in 1943, Furukawa[164] in 1962, and Kruh[165] in 1962 while the Fourier analysis of X-ray data was reviewed by Paalman and Pings[166] in 1963.

Neutron diffraction has an advantage over X-ray diffraction in that slow neutron scattering from a nucleus is isotropic with no angularly dependent form factor. Elsasser[167] first suggested in 1936 that neutrons would be diffracted by crystals and an experimental demonstration of this was given by Halban and Preiswerk[168] and by Mitchell and Powers,[169] both in 1936. However, it wasn't until 1950 that neutron diffraction studies of liquids were carried out by Chamberlain[170] on liquid sulpher, lead, and bismuth. Liquid lead and bismuth were again studied by Sharrah and Smith[171] in 1953. Henshaw, Hurst, and Pope[172] measured the neutron angular distributions of liquid nitrogen, oxygen, and argon in 1953, with liquid argon receiving further study by Henshaw[173] in 1957. An interesting observation and discussion of differences between X-ray and neutron-derived radial distribution functions due to normalization has recently been given by Rahman.[174] A pertinent paper on neutron diffraction counting errors has been given by Schlup.[175]

The quantity measured in a neutron angular distribution is the relative cross section $\frac{d\sigma}{d\Omega} = I\left(\frac{4\pi}{\lambda_i}\sin\frac{\theta}{2}\right)$ as a function of θ for a given E_i chosen such that the neutron wavelength is of the order of interatomic spacings in the substance of interest. Most measurements use neutrons of energy E_i such that $\lambda \simeq 1Å$.

The data are usually reduced using either the formula,

$$4\pi r^2\left[\rho(r)-\rho_\infty\right] = \frac{2r}{\pi}\int_0^\infty s\, i(s)\sin(rs)\,ds, \qquad \text{(E.1)}$$

or

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_\infty} \int_0^\infty s\, i(s) \sin(rs)\, ds, \tag{E.2}$$

which relates the density $\rho(r)$ or the radial distribution function $g(r)$ to the measured quantity $i(s)$,

$$i(s) = \frac{I(s) - I(\infty)}{I(\infty)} \tag{E.3}$$

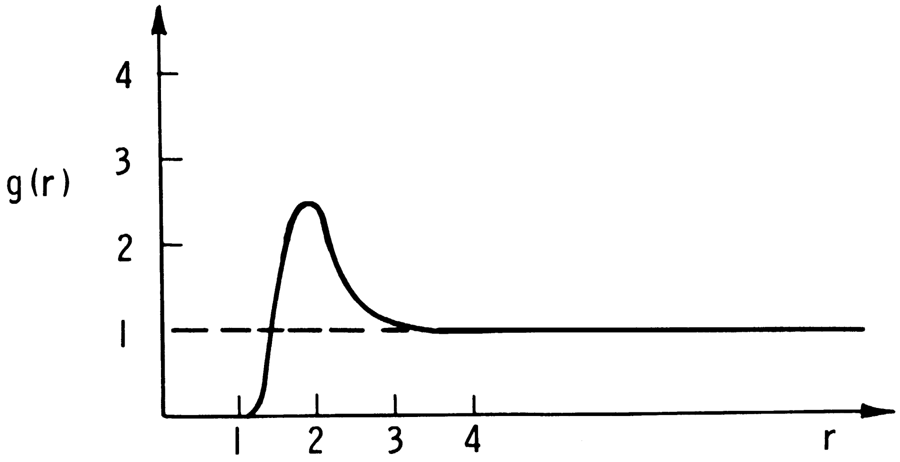
where $S = \frac{4\pi}{\lambda_i} \sin\frac{\theta}{2}$, ρ_∞ is the average density, and where $g(r)\,d^3r$ is the probability that, given an atom at the origin, a distinct one will be found simultaneously in d^3r about $\underline{r}$. The radial distribution depends on density and temperature.

One feature of the liquid state, namely, the presence of "short-range order," can best be visualized with the aid of Fig. 11. The $g(r)$ in the solid state is obtained by averaging over different directions outward from the central molecule since spherical symmetry, assumed for $g(r)$, is lacking. These peaks in $g(r)$ for the solid correspond, as r increases, to first neighbors, second neighbors, etc.

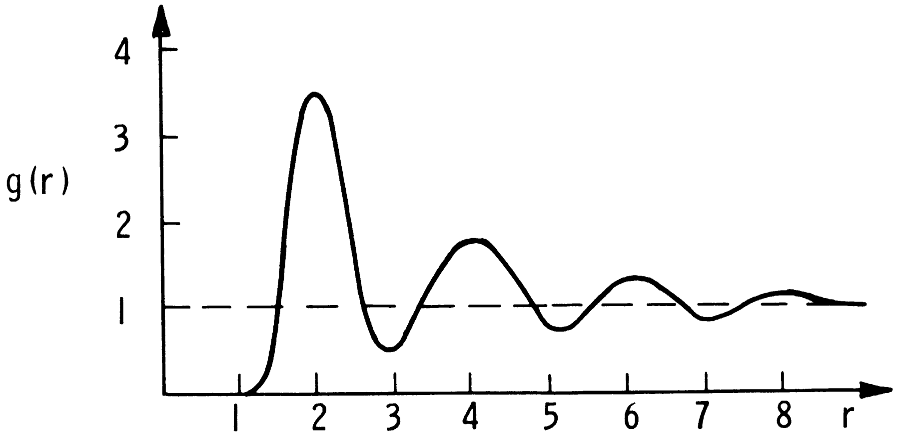
The peaks in the liquid are smeared-out remnants of the relatively sharper peaks in $g(r)$ in the solid. Thus the liquid has a certain amount of short-range ordering. The fact that in a liquid $g(r) \rightarrow 1$ for large r, as it does in a gas, describes the absence of "long-range order" seen in a solid. The quantity

$$\int_A^B 4\pi r^2 g(r)\, dr,$$

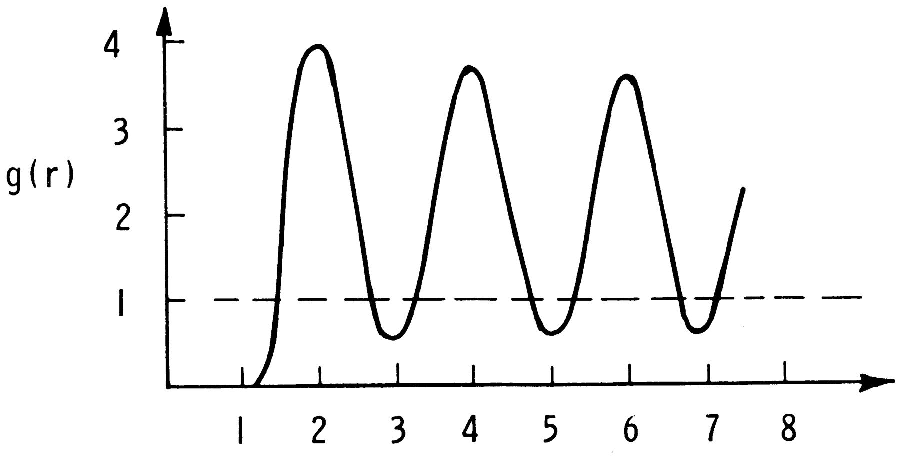
where integration is over one peak in $g(r)$ for a liquid, is the "liquid coordination number" giving the number of neighbors in that



(a) DILUTE GAS



(b) LIQUID



(c) SOLID

Figure 11. Schematic radial distribution functions for dilute gas, liquid, and solid.

coordination "shell." This number, in general, decreases with increasing temperature.

In the remainder of this appendix we calculate an angular distribution for a "micro-crystalline" model of a liquid and compare it with the experimental angular distribution for argon. In so doing we are able to illustrate the character of short-range ordering in simple liquids.

We consider the liquid as composed of small clusters of atoms. The atoms in each cluster are ordered as in a crystal, the number of atoms in a cluster varying from cluster to cluster. There are also a number of single atoms, temporarily "between" clusters, but ready for formation into a cluster which move with "gas-like" freedom. The clusters, then, being pictured as having a finite lifetime, but continually "reproduce" themselves. This model corresponds to the significant structure theory[146] (though other models may also).

We now note the different roles of direct and interference scattering in determining the shape of the measured angular distribution. This can best be seen with the aid of Fig. 12. The direct scattering is nearly constant with angle. However, the structure we hope to describe by either a free gas model or a harmonic crystal can be seen to influence the outer scattering, which depends for its description upon a detailed knowledge of position correlations and their time dependences. If we assume the motions of atoms in the clusters are harmonic vibrations about temporary equilibrium positions and also take into account the fact that inelastic effects are small in the interference scattering, the cross section for these atoms is

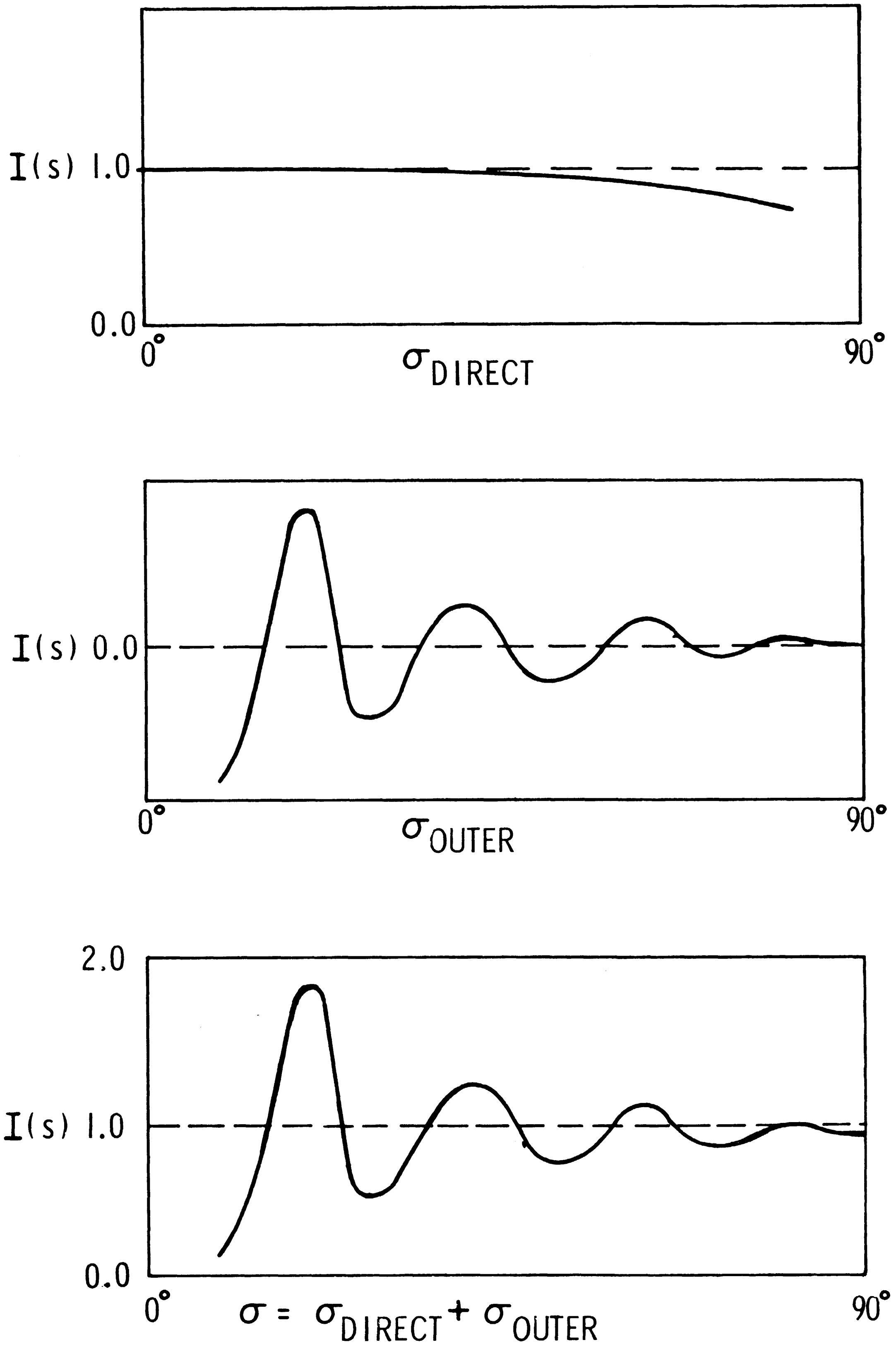


Figure 12. Schematic neutron angular distribution showing intensity versus scattering angle.

$$\frac{d\sigma}{d\Omega} = a_c^2 \, \frac{e^{-2W_0}}{N} \sum_{\ell}^{N} \sum_{\ell' \neq \ell}^{N-1} \left\langle e^{i \underline{K}_0 \cdot \underline{R}_{\ell'\ell}} \right\rangle_{\Omega}, \qquad \text{(E.4)}$$

where a_c is the coherent scattering length, e^{-2W_0} is the Debye-Waller factor for momentum transfer $|\underline{K}_0| = 2k_i \sin\frac{\theta}{2}$ and $\underline{R}_{\ell'\ell} = \underline{R}_{\ell} - \underline{R}_{\ell'}$. We separate the double sum as follows:

$$\frac{1}{N} \sum_{\ell} \sum_{\ell' \neq \ell} = \frac{1}{n} \sum_{i} \left[\sum_{\ell}^{N_i} \sum_{\ell' \neq \ell}^{N_i - 1} + \sum_{\ell}^{N_i} \sum_{\ell'}^{N - N_i} \right], \qquad \text{(E.5)}$$

where n is the number of clusters of atoms in the liquid. The average $\langle \, \rangle_{\Omega}$ over orientations can be accomplished assuming a random distribution of the directions $\underline{R}_{\ell'\ell}$, as follows:

$$\left\langle e^{i \underline{K}_0 \cdot \underline{R}_{\ell'\ell}} \right\rangle_{\Omega} = \frac{1}{2} \int_{-1}^{1} d\mu \, e^{i K_0 R_{\ell'\ell} \mu} = \frac{\sin K_0 R_{\ell'\ell}}{K_0 R_{\ell'\ell}}, \qquad \text{(E.6)}$$

where $\mu = \cos\varphi$ and φ is the angle between $\underline{K}_0$ and $\underline{R}_{\ell'\ell}$. Thus we find

$$\frac{d\sigma_h}{d\Omega} \cong a_c^2 \, \frac{e^{-2W_0}}{n} \sum_{\ell}^{N_i} \sum_{\ell' \neq \ell}^{N_i - 1} \frac{\sin K_0 R_{\ell'\ell}}{K_0 R_{\ell'\ell}}, \qquad \text{(E.7)}$$

since the terms neglected will have a very small contribution. We estimate the cross section contribution of the "free" atoms to be given by[176]

$$\begin{aligned} \frac{d\sigma_f}{d\Omega} = a_c^2 \Big\{ & -\frac{3D}{K_0 d} j_1(K_0 d) + \frac{3D^2}{16} \Big[24(K_0^2 d^2 - 1)\cos 2K_0 d \\ & - 48 K_0 d \sin 2K_0 d + (5K_0^4 d^4 + 12 K_0^2 d^2 + 24) \qquad \text{(E.8)} \\ & (\times) \cos K_0 d + (4K_0^2 d^2 + 24 K_0 d) \sin K_0 d \Big] \Big\}, \end{aligned}$$

with

$$D = \frac{4}{3}\pi d^3 \rho_\infty ,$$
$$j_1(K_0 d) = \frac{\sin(K_0 d) - K_0 d \cos(K_0 d)}{(K_0 d)^2} , \tag{E.9}$$

where we have assumed atoms interact as hard spheres of diameter d and have made an expansion to first order in the density. We will estimate the relative contributions of solid-like structures and single atoms as in the significant structure theory, namely, V_S/V gives the fractional contribution of $\frac{d\sigma_h}{d\Omega}$, and $\frac{V-V_S}{V}$ the contribution of $\frac{d\sigma_f}{d\Omega}$, where V_s is the volume of the solid at the melting point and V is the volume of the liquid. We will choose $V = 1.12\, V_S$.

We now present in Fig. 13 calculations for argon of the angular distribution:

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma_{\text{DIRECT}}}{d\Omega} + \frac{d\sigma_{\text{OUTER}}}{d\Omega}$$

with

$$\frac{d\sigma_{\text{OUTER}}}{d\Omega} = .89\, \frac{d\sigma_h}{d\Omega} + .11\, \frac{d\sigma_f}{d\Omega}$$

where $\frac{d\sigma_h}{d\Omega}$ is given by (E.7) with E_i = .0757 ev and the lattice spacing of the solid, 5.44Å, where $\frac{d\sigma_f}{d\Omega}$ is given by (E.8) with $\rho_\infty = 2.13 \times 10^{-2}$ atoms/Å^3, and where N_i is chosen first as 14 atoms and then 63 atoms arranged in a face-centered cubic structure. Also shown is the experimental curve by Henshaw[173] at 84°K. We note that the first maximum is poorly predicted using 14 atoms, as is the first minimum. Increasing the short-range ordering distance to include 63 atoms allows an improvement in the first maximum. However, little

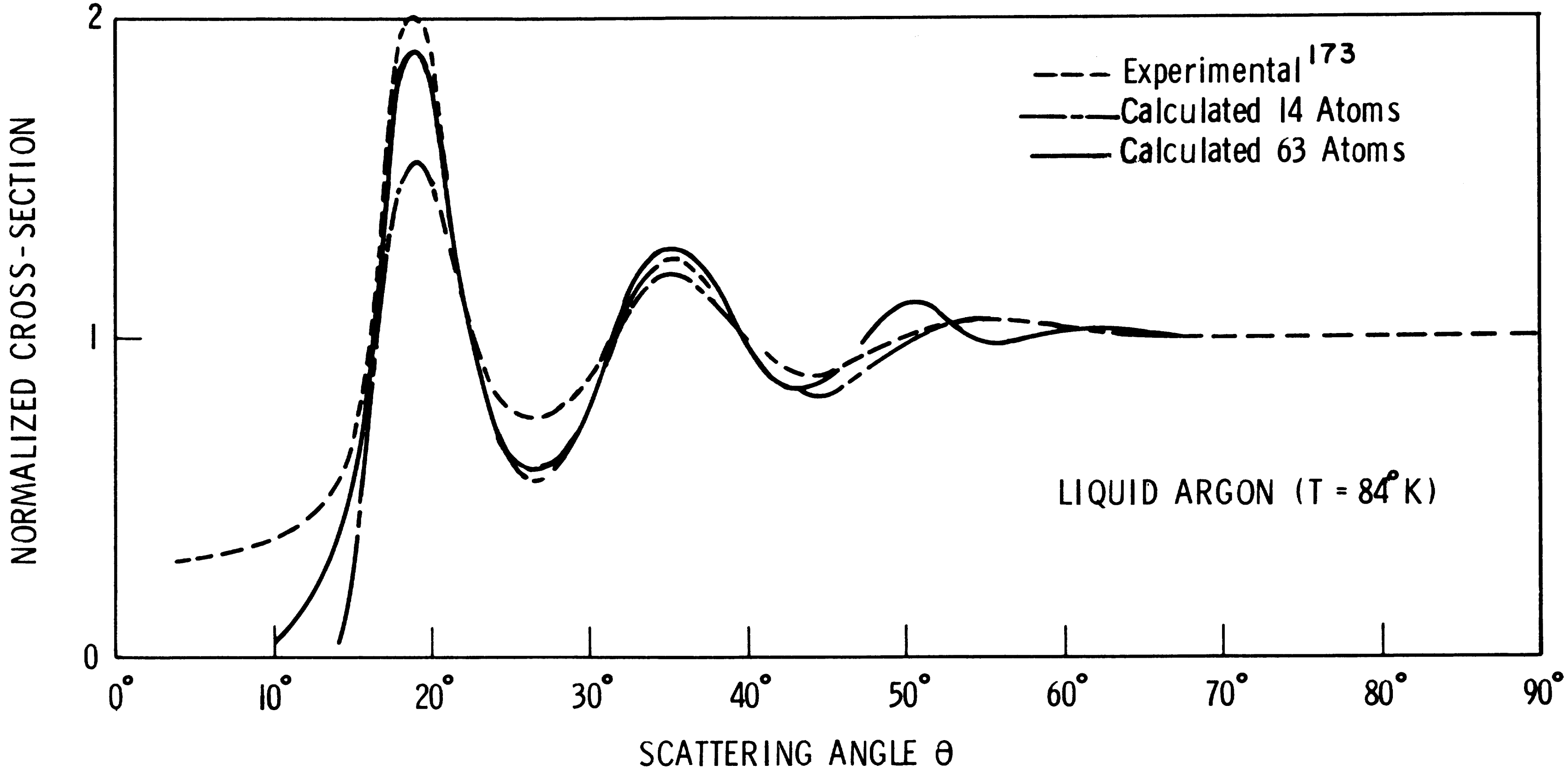


Figure 13. Neutron angular distribution for liquid argon at 84°K.

improvement occurs for the first minimum. More striking is the fact that the second and third maxima become progressively worse.

The conclusion drawn from this is that in simple liquids like those of the noble elements short-range ordering is not crystal-like even three coordination shells into the surrounding liquid, the loosening of the structure and the change in positions destroying the order over distances as small as three or four nearest neighbor distances.

Similar results apply to the structure of liquid metals, in general, but they occupy a special class. Simple liquids consist of spherically symmetric, non-dipolar particles with interactions which are non-directional and non-saturating van der Waals forces. But in liquid metals the intermolecular forces are caused by the collective interactions between ion cores and free electrons, and thus the interatomic pair potential has a long-range oscillatory character[177] as has been observed in crystalline metals.

The application of X-ray and neutron diffraction to polyatomic liquids yields little of the same kind of information because the interpretation of atomic distributions in terms of molecular distributions is very difficult.[165]

But the inference has been drawn[165] that a quasi-crystalline structure exists for those liquids in which the correlation between molecules is very strong because of the presence of a specific orientation-dependent force, such as in polar or hydrogen bonded liquids.

APPENDIX F

ANGULAR MOMENTUM OPERATORS AND HAMILTONIAN FOR RIGID MOLECULES

When a rigid body undergoes an arbitrary rotation, rotation about any axis gives rise to an angular velocity along that axis. Hence, the angular velocity in terms of Euler angles is (see Fig. 2),

$$\underline{\omega} = \dot{\theta}_1 \underline{e}_3 + \dot{\theta}_2 \underline{e}_2''' + \dot{\theta}_3 \underline{e}_3'' , \tag{F.1}$$

or in the space-fixed system

$$\underline{\omega} = \dot{\theta}_1 \underline{e}_3 + \dot{\theta}_2 R_{2j}(\theta_1) \underline{e}_j + \dot{\theta}_3 R_{3j}(\theta_2) R_{jk}(\theta_1) \underline{e}_k , \tag{F.2}$$

where

$$R(\theta_1) = \begin{pmatrix} c_1 & s_1 & 0 \\ -s_1 & c_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} ; \quad R(\theta_2) = \begin{pmatrix} c_2 & 0 & -s_2 \\ 0 & 1 & 0 \\ s_2 & 0 & c_2 \end{pmatrix} , \tag{F.3}$$

and $c_i \equiv \cos\theta_i$, $s_i \equiv \sin\theta_i$. Consider an infinitesimal rotation of a function $f(\theta_i)$ about the space axis $\underline{e}_j$ by an amount β_j ,

$$Rf(\theta_i) = g(\theta_i') \equiv f(\theta_i + \Delta_i) \tag{F.4}$$

where

$$\Delta_i = \beta_j \frac{\partial \theta_i}{\partial \beta_j} \tag{F.5}$$

is the change in θ_i due to the rotation. Since Δ_i is small we may expand

$$f(\theta_i+\Delta_i) \simeq f(\theta_i) + \Delta_i \frac{\partial f(\theta_i)}{\partial \theta_i} ,$$

$$= f(\theta_i) + \beta_j \frac{\partial \theta_i}{\partial \beta_j} \frac{\partial f(\theta_i)}{\partial \theta_i} . \qquad \text{(F.6)}$$

Now the angular momentum operator L_j is given by

$$L_j = -i\hbar \lim_{\beta_j \to 0} \left\{ \frac{g(\theta_i') - f(\theta_i)}{\beta_j f(\theta_i)} \right\} ,$$

$$= -i\hbar \left(\frac{\partial \theta_i}{\partial \beta_j} \frac{\partial}{\partial \theta_i} \right) = -i\hbar \left(\frac{\partial \dot{\theta}_i}{\partial \omega_j} \frac{\partial}{\partial \theta_i} \right) = -i\hbar \Omega_{ji} \frac{\partial}{\partial \theta_i} , \qquad \text{(F.7)}$$

where we need to determine

$$\Omega_{ji} = \frac{\partial \dot{\theta}_i}{\partial \omega_j} \qquad \text{(F.8)}$$

We may treat (F.2) as a matrix equation of the form, $\omega_j = B_{ji} \dot{\theta}_i$, from which we can find $B^{-1}_{ij} = \frac{\partial \dot{\theta}_i}{\partial \omega_j}$ and hence $\Omega_{ji} = (B^{-1}_{ij})^T$. From (F.2) and (F.3) we find

$$B = \begin{pmatrix} 0 & -S_1 & S_2 C_1 \\ 0 & C_1 & S_2 S_1 \\ 1 & 0 & C_2 \end{pmatrix} , \quad B^{-1} = \begin{pmatrix} -\frac{C_1 C_2}{S_2} & -\frac{S_1 C_2}{S_2} & 1 \\ -S_1 & C_1 & 0 \\ \frac{C_1}{S_2} & \frac{S_1}{S_2} & 0 \end{pmatrix} , \qquad \text{(F.9)}$$

and

$$\Omega = \begin{pmatrix} -\frac{C_1 C_2}{S_2} & -S_1 & \frac{C_1}{S_2} \\ -\frac{S_1 C_2}{S_2} & C_1 & \frac{S_1}{S_2} \\ 1 & 0 & 0 \end{pmatrix} . \qquad \text{(F.10)}$$

Hence, the angular momentum operators in the space system are:

$$L_x = -i\hbar\left\{-\frac{\cos\psi}{\sin\theta}\left(\cos\theta\frac{\partial}{\partial\psi}+\frac{\partial}{\partial\varphi}\right)-\sin\psi\frac{\partial}{\partial\theta}\right\},$$

$$L_y = -i\hbar\left\{-\frac{\sin\psi}{\sin\theta}\left(\cos\theta\frac{\partial}{\partial\psi}-\frac{\partial}{\partial\varphi}\right)+\cos\psi\frac{\partial}{\partial\theta}\right\}, \qquad \text{(F.11)}$$

$$L_z = -i\hbar\frac{\partial}{\partial\psi}.$$

To find the angular momentum operators in the body system note that

$$L_j' = R_{jk}L_k = R_{jk}\Omega_{ki}\left(-i\hbar\frac{\partial}{\partial\theta_i}\right), \qquad \text{(F.12)}$$

and hence

$$L_j' = -i\hbar\,\Omega_{ji}'\frac{\partial}{\partial\theta_i}, \qquad \text{(F.13)}$$

where

$$\Omega_{ji}' = R_{jk}\Omega_{ki}, \qquad \text{(F.14)}$$

and

$$R = R(\theta_3)R(\theta_2)R(\theta_1) = \begin{pmatrix} C_3C_2C_1 - S_3S_1 & C_3C_2S_1 + S_3C_1 & -C_3S_2 \\ -S_3C_2C_1 - C_3S_1 & -S_3C_2S_1 + C_3C_1 & S_3S_2 \\ S_2C_1 & S_2S_1 & C_2 \end{pmatrix}. \qquad \text{(F.15)}$$

We find

$$\Omega' = \begin{pmatrix} -\frac{c_3}{s_2} & s_3 & \frac{c_2 c_3}{s_2} \\ \frac{s_3}{s_2} & c_3 & -\frac{c_2 s_3}{s_2} \\ 0 & 0 & 1 \end{pmatrix}, \tag{F.16}$$

and hence

$$\begin{aligned} L'_x &= -i\hbar\left\{-\frac{\cos\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\varphi}\right) + \sin\varphi\frac{\partial}{\partial\theta}\right\}, \\ L'_y &= -i\hbar\left\{\frac{\sin\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\varphi}\right) + \cos\varphi\frac{\partial}{\partial\theta}\right\}, \\ L'_z &= -i\hbar\frac{\partial}{\partial\varphi}. \end{aligned} \tag{F.17}$$

Throughout this dissertation the Euler angles are defined with respect to a right-handed coordinate system. A different but equivalent method of obtaining the angular momentum operators is presented in Appendix H in the context of an internal rotation problem. In some of the literature, e.g., Goldstein,[178] Margenau and Murphy,[179] Wang,[180] and Van Winter,[57] the second rotation is about the $\underline{e}_1'''$ axis rather than the $\underline{e}_2'''$ axis used here.

The Hamiltonian operator is given by (3.2), where using L'_j, we find

$$
\begin{aligned}
-\frac{2}{\hbar^2 C} H_{FR} = a\Bigg\{ & \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right]\Bigg\} \\
& + \frac{\partial^2}{\partial\varphi^2} \\
& + b\Bigg\{\cos 2\varphi\Bigg[-\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right) \\
& \qquad - \frac{\partial^2}{\partial\varphi^2} + 2\cot\theta\frac{\partial}{\partial\theta}\Bigg] \\
& + \sin 2\varphi\Bigg[-\frac{2}{\sin\theta}\left(\frac{\partial^2}{\partial\theta\partial\psi} - \cos\theta\frac{\partial^2}{\partial\theta\partial\varphi}\right) \\
& \qquad + \frac{2\cos\theta}{\sin^2\theta}\frac{\partial}{\partial\psi} - \left(1 + 2\cot^2\theta\right)\frac{\partial}{\partial\varphi}\Bigg]\Bigg\}.
\end{aligned}
\tag{F.18}
$$

APPENDIX G

INTERNAL ROTATIONAL KINETIC ENERGY AND ANGULAR MOMENTUM FOR GASES AND NORMAL LIQUIDS

Let $\underline{r}_j$ denote the position vector from the center of mass of the molecule to the j^{th} atom in the symmetric top group, let $\underline{\sigma}_j$ denote the position vector of the j^{th} atom from the center of mass of the symmetric top alone, let the vector from the center of mass of the molecule to the center of mass of the top be ρ, and let the position vector of the i^{th} atom in the frame be denoted by $\underline{r}_i$. Then

$$\underline{r}_j = \rho + \underline{\sigma}_j, \tag{G.1}$$

and the classical kinetic energy can be written

$$T = \frac{1}{2}\sum_i m_i \dot{\underline{r}}_i \cdot \dot{\underline{r}}_i + \frac{1}{2}\sum_j m_j \dot{\underline{r}}_j \cdot \dot{\underline{r}}_j. \tag{G.2}$$

Noting that

$$\dot{\underline{r}}_i = \underline{\omega} \times \underline{r}_i, \quad \dot{\underline{r}}_j = (\underline{\omega} \times \underline{r}_j) + (\dot{\underline{\alpha}} \times \underline{\sigma}_j), \tag{G.3}$$

where $\underline{\omega}$ is the angular velocity of the over-all free rotation of the molecule, and $\dot{\underline{\alpha}}$ is the angular velocity of the internal rotation, (G.2) can be rewritten as

$$\begin{aligned} T &= \frac{1}{2}\sum_i m_i (\underline{\omega} \times \underline{r}_i)^2 + \frac{1}{2}\sum_j m_j \left[(\underline{\omega} \times \underline{r}_j) + (\dot{\underline{\alpha}} \times \underline{\sigma}_j)\right]^2, \\ &= \frac{1}{2}\sum_i m_i \left[r_i^2 \omega^2 - (\underline{\omega} \cdot \underline{r}_i)^2\right] + \frac{1}{2}\sum_j m_j \left[r_j^2 \omega^2 - (\underline{\omega} \cdot \underline{r}_j)^2\right] \\ &\quad + \frac{1}{2}\sum_j m_j \left[\sigma_j^2 \dot{\alpha}^2 - (\underline{\sigma}_j \cdot \dot{\underline{\alpha}})^2\right] + \sum_j m_j (\underline{\omega} \times \underline{r}_j) \cdot (\dot{\underline{\alpha}} \times \underline{\sigma}_j). \end{aligned} \tag{G.4}$$

The first two terms represent the kinetic energy of the over-all rigid rotation of the molecule, and can be written as $\frac{1}{2}\sum_{lk} I_{lk}\omega_l\omega_k$ where I_{lk} is the lk^th element of the inertia tensor of the entire molecule. The third term may be expressed as $\frac{1}{2} I_a \dot{\alpha}^2$ where I_a is the moment of inertia of the top about its axis of symmetry. The last term of (G.4) simplifies as

$$\sum_j m_j(\underline{\omega}\times\underline{r}_j)\cdot(\dot{\underline{\alpha}}\times\underline{\sigma}_j) = \sum_j m_j\left\{\left[(\underline{\rho}+\underline{\sigma}_j)\cdot\underline{\sigma}_j\right](\underline{\omega}\cdot\dot{\underline{\alpha}}) - (\underline{\omega}\cdot\underline{\sigma}_j)\left[(\underline{\rho}+\underline{\sigma}_j)\cdot\dot{\underline{\alpha}}\right]\right\},$$

$$= \sum_j m_j\left[\sigma_j^2(\underline{\omega}\times\dot{\underline{\alpha}}) - (\underline{\omega}\cdot\underline{\sigma}_j)(\underline{\sigma}_j\cdot\dot{\underline{\alpha}})\right], \qquad (G.5)$$

since

$$\sum_j m_j\underline{\sigma}_j = 0. \qquad (G.6)$$

By using a coordinate system attached to the top with the z-axis along the axis of symmetry, and the origin located at the center of mass of the top, we have

$$\underline{\sigma}_j = x_j\underline{i} + y_j\underline{j} + z_j\underline{k}, \qquad (G.7)$$

and

$$\sum_j m_j x_j z_j = \sum_j m_j y_j z_j = 0. \qquad (G.8)$$

Then (G.5) becomes

$$\sum_j m_j\left[(x_j^2+y_j^2+z_j^2)(\underline{\omega}\cdot\dot{\underline{\alpha}}) - (\omega_x x_j + \omega_y y_j + \omega_z z_j)z_j|\dot{\underline{\alpha}}|\right]$$

$$= \sum_j m_j\left[(x_j^2+y_j^2+z_j^2)(\underline{\omega}\cdot\dot{\underline{\alpha}}) - \omega_z z_j^2|\dot{\underline{\alpha}}|\right], \qquad (G.9)$$

$$= \sum_j m_j(x_j^2+y_j^2)(\underline{\omega}\cdot\dot{\underline{\alpha}}) = I_a(\underline{\omega}\cdot\dot{\underline{\alpha}}).$$

Therefore, the kinetic energy becomes

$$T=\frac{1}{2}\sum_{lk} I_{lk}\omega_l\omega_k+\frac{1}{2}I_a\dot{\alpha}^2+I_a(\underline{\omega}\cdot\underline{\dot{\alpha}}). \tag{G.10}$$

The classical angular momentum is given by

$$\begin{aligned}\underline{L}&=\sum_i m_i(\underline{r}_i\times\underline{\dot{r}}_i)+\sum_j m_j'(\underline{r}\times\underline{\dot{r}}_j'),\\ &=\sum_i m_i(\underline{r}_i\times(\underline{\omega}\times\underline{r}_i))+\sum_j m_j'(\underline{r}_j'\times(\underline{\omega}\times\underline{r}_j'))+\sum_j m_j'(\underline{r}_j'\times(\underline{\dot{\alpha}}\times\underline{\sigma}_j')).\end{aligned} \tag{G.11}$$

The first two terms stand for the angular momentum of the over-all rigid rotation of the entire molecule, which can be written as $\mathbb{I}\cdot\underline{\omega}$ where $\mathbb{I}$ is the inertia tensor of the molecule. In order to simplify the last term, use is made of the fact that $\underline{\sigma}_j'$ is a vector measured from the center of mass of the top and that the axis of internal rotation of the top is a principal axis of the top. Then

$$\begin{aligned}\sum_j m_j'[\underline{r}_j'\times(\underline{\dot{\alpha}}\times\underline{\sigma}_j')]&=\sum_j m_j'[(\underline{\rho}+\underline{\sigma}_j')\times(\underline{\dot{\alpha}}\times\underline{\sigma}_j')]\\ &=\sum_j m_j'[\underline{\sigma}_j'\times(\underline{\dot{\alpha}}\times\underline{\sigma}_j')]\\ &=\sum_j m_j'[\sigma_j'^2\underline{\dot{\alpha}}-(\underline{\sigma}_j'\cdot\underline{\dot{\alpha}})\underline{\sigma}_j']\\ &=\sum_j m_j'[\sigma_j'^2|\underline{\dot{\alpha}}|\underline{k}-z_j'^2|\underline{\dot{\alpha}}|\underline{k}]\\ &=I_a\underline{\dot{\alpha}}\end{aligned} \tag{G.12}$$

So that (G.11) reduces to

$$\underline{L}=\mathbb{I}\cdot\underline{\omega}+I_a\underline{\dot{\alpha}}, \tag{G.13}$$

Hence, in the IAM where $\underline{L}_a'$ is along z,

$$\begin{aligned}L_x'&=I_x\omega_x\\ L_y'&=I_y\omega_y\\ L_z'&=I_z\omega_z+I_a\dot{\alpha}\end{aligned} \tag{G.14}$$

and

$$\begin{aligned} L'^2 &\equiv L'^2_x + L'^2_y + L'^2_z \\ &= I_x^2 \omega'^2_x + I_y^2 \omega'^2_y + I_z^2 \omega'^2_z + 2 I_z I_a \omega'_z \dot{\alpha} + I_a^2 \dot{\alpha}^2 . \end{aligned} \tag{G.15}$$

Now the transformation to the internal rotation coordinate system is accomplished with (3.48), so that we have

$$L^{i\,2} = L^{i\,2}_x + L^{i\,2}_y + L^{i\,2}_z = L'^2_x + L'^2_y + L'^2_z = L'^2 . \tag{G.16}$$

APPENDIX H

INTERNAL ROTATIONAL ANGULAR MOMENTUM OPERATORS AND HAMILTONIAN

Consider a set of axes fixed in space and a set of axes fixed in an arbitrary body of interest. The set of axes fixed in space and the body-fixed system can be brought into coincidence by three successive rotations, viz. (adopting the summation convention)

$$\underline{e}_i''' = R_{ij}(\theta_1)\underline{e}_j, \qquad 0 \leq \theta_1 < 2\pi$$

$$\underline{e}_i'' = R_{ij}(\theta_2)R_{jk}(\theta_1)\underline{e}_k, \qquad 0 \leq \theta_2 < \pi$$

$$\underline{e}_i' = R_{ij}(\theta_3)R_{jk}(\theta_2)R_{k\ell}(\theta_1)\underline{e}_\ell = R_{i\ell}\,\underline{e}_\ell, \qquad 0 \leq \theta_3 < 2\pi$$

where $\underline{e}_i$ and $\underline{e}_i'$ are respectively the space and body axes, and the angles ($\theta_1, \theta_2, \theta_3$) are called Euler angles.

In the internal rotation problem, the top-fixed axes require still another rotation by an angle θ_4 about $\underline{e}_3'$, the first three rotations being about $\underline{e}_3$, $\underline{e}_2'''$ and $\underline{e}_3''$ respectively (See Fig. 14). That is, the frame-fixed system is the "body-fixed" system referred to above and the top-fixed system is given by

$$\underline{e}_i'^{\,top} = R_{ij}(\theta_4)R_{jk}(\theta_3)R_{k\ell}(\theta_2)R_{\ell m}(\theta_1)\underline{e}_m$$

$$= R_{ij}(\theta_4)R_{jm}\,\underline{e}_m, \qquad 0 \leq \theta_4 < 2\pi$$

When the body undergoes an arbitrary rotation, rotation about a given axis gives rise to an angular velocity along that axis. The angular velocity $\underline{\omega}$ for the arbitrary rotation expressed in terms of the four

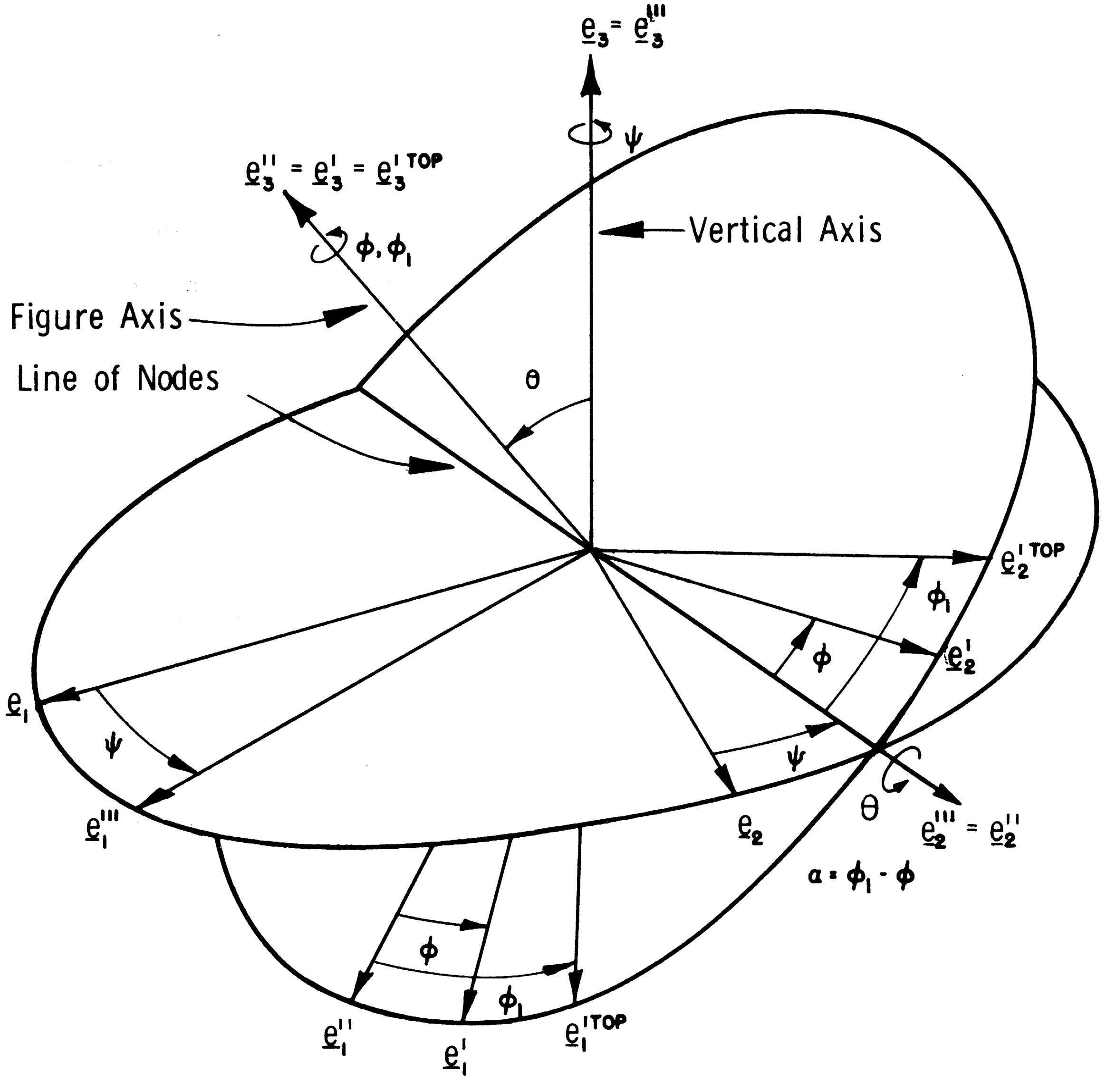


Figure 14. Euler angles $(\psi\theta\varphi\alpha)$ for internal rotation.

Euler angles is

$$\underline{\omega} = \dot{\theta}_1 \underline{e}_3 + \dot{\theta}_2 \underline{e}_2''' + \dot{\theta}_3 \underline{e}_3'' + \dot{\theta}_4 \underline{e}_3' . \tag{H.1}$$

Expressing the angular velocity in the body system then gives

$$\begin{aligned} \underline{\omega}' = {} & \dot{\theta}_1 R^{-1}_{3j}(\theta_2) R^{-1}_{jk}(\theta_3) R^{-1}_{k\ell}(\theta_4) \underline{e}_\ell' \\ & + \dot{\theta}_2 R^{-1}_{2j}(\theta_3) R^{-1}_{jk}(\theta_4) \underline{e}_k' + \dot{\theta}_3 R^{-1}_{3j}(\theta_4) \underline{e}_j' + \dot{\theta}_4 \underline{e}_3' , \end{aligned} \tag{H.2}$$

where

$$R(\theta_i) = \begin{pmatrix} C_i & S_i & 0 \\ -S_i & C_i & 0 \\ 0 & 0 & 1 \end{pmatrix}, i=1,3,4 ; \quad R(\theta_2) = \begin{pmatrix} C_2 & 0 & -S_2 \\ 0 & 1 & 0 \\ S_2 & 0 & C_2 \end{pmatrix},$$

$$R^{-1}(\theta_i) = \begin{pmatrix} C_i & -S_i & 0 \\ S_i & C_i & 0 \\ 0 & 0 & 1 \end{pmatrix}, i=1,3,4 ; \quad R^{-1}(\theta_2) = \begin{pmatrix} C_2 & 0 & S_2 \\ 0 & 1 & 0 \\ -S_2 & 0 & C_2 \end{pmatrix},$$

and $C_i \equiv \cos\theta_i , \; S_i \equiv \sin\theta_i .$

As an illustration of the procedure of quantizing the classical Hamiltonian to achieve the quantum mechanical Hamiltonian, consider the free symmetric molecule case in the IAM. The components of the angular velocity in the frame-fixed system are found from (H.2) with $\theta_1 = \psi$, $\theta_2 = \theta$, $\theta_3 = \varphi$, $\theta_4 = \rho\alpha$, to be

$$\begin{aligned} \omega_x' = {} & \dot{\theta} \sin\varphi \cos\rho\alpha + \dot{\theta} \cos\varphi \sin\rho\alpha \\ & + \dot{\psi} \sin\theta \sin\varphi \sin\rho\alpha - \dot{\psi} \sin\theta \cos\varphi \cos\rho\alpha , \\ \omega_y' = {} & \dot{\theta} \cos\varphi \cos\rho\alpha - \dot{\theta} \sin\varphi \sin\rho\alpha \\ & + \dot{\psi} \sin\theta \sin\varphi \cos\rho\alpha + \dot{\psi} \sin\theta \cos\varphi \sin\rho\alpha , \\ \omega_z' = {} & \dot{\varphi} + \dot{\psi} \cos\theta + \rho\dot{\alpha} , \end{aligned} \tag{H.3}$$

where $\rho = I_a / I_z$. However, we want to make the transformation $\varphi' = \varphi + \rho\alpha$ to the internal rotation coordinate system. Hence, the components of the angular velocity become

$$\begin{aligned} \omega_x' &= \dot{\theta}\sin\varphi' - \dot{\psi}\sin\theta\cos\varphi', \\ \omega_y' &= \dot{\theta}\cos\varphi' + \dot{\psi}\sin\theta\sin\varphi', \\ \omega_z' &= \dot{\varphi}' + \dot{\psi}\cos\theta, \end{aligned} \tag{H.4}$$

and the kinetic energy (G.10) becomes

$$\begin{aligned} T = {}& \tfrac{1}{2}I(\dot{\theta}\sin\varphi' - \dot{\psi}\sin\theta\cos\varphi')^2 + \tfrac{1}{2}I(\dot{\theta}\cos\varphi' + \dot{\psi}\sin\theta\sin\varphi')^2 \\ & + \tfrac{1}{2}I_z(\dot{\varphi}' + \dot{\psi}\cos\theta)^2 + \tfrac{1}{2}I_a\dot{\alpha}^2 + I_a(\varphi' + \dot{\psi}\cos\theta)\dot{\alpha}. \end{aligned} \tag{H.5}$$

But application of the Nielsen transformation (See Eq. [3.44]) reduces this to

$$T = \tfrac{1}{2}I\dot{\theta}^2 + \tfrac{1}{2}I\sin^2\theta\,\dot{\psi} + \tfrac{1}{2}I_z(\dot{\varphi}' + \dot{\psi}\cos\theta)^2 + \tfrac{1}{2}rI_a\dot{\alpha}^2, \tag{H.6}$$

so that the <u>line element</u> $ds^2 \equiv 2T\,dt^2$ becomes

$$ds^2 = I\,d\theta^2 + I\sin^2\theta\,d\psi^2 + I_z(d\varphi' + \cos\theta\,d\psi)^2 + rI_a\,d\alpha^2. \tag{H.7}$$

Then writing

$$ds^2 = \sum_{ij} g_{ij}\,dq_i\,dq_j\,; \quad q_1 = \psi,\ q_2 = \theta,\ q_3 = \varphi',\ q_4 = \alpha, \tag{H.8}$$

the quantum mechanical kinetic energy operator is given by

$$-\frac{\hbar^2}{2}\frac{1}{g^{1/2}}\sum_i \frac{\partial}{\partial q_i}\left(g^{1/2}\sum_j g^{ij}\frac{\partial}{\partial q_j}\right).$$

On identifying the g_{ij} from (H.7) we find

$$[g_{ij}] = \begin{bmatrix} I\sin^2\theta + I_z\cos^2\theta & 0 & I_z\cos\theta & 0 \\ 0 & I & 0 & 0 \\ I_z\cos\theta & 0 & I_z & 0 \\ 0 & 0 & 0 & rI_a \end{bmatrix}. \tag{H.9}$$

Then

$$g \equiv \mathrm{Det}(g_{ij}) = rI_a I^2 I_z \sin^2\theta, \tag{H.10}$$

and

$$[g^{ij}] = \begin{bmatrix} \frac{1}{I\sin^2\theta} & 0 & \frac{-\cos\theta}{I\sin^2\theta} & 0 \\ 0 & \frac{1}{I} & 0 & 0 \\ \frac{-\cos\theta}{I\sin^2\theta} & 0 & \frac{1}{I_z} + \frac{\cos^2\theta}{I\sin^2\theta} & 0 \\ 0 & 0 & 0 & \frac{1}{rI_a} \end{bmatrix} \tag{H.11}$$

Therefore,

$$\begin{aligned} T = -\frac{\hbar^2}{2\sin\theta}\Big\{ & \frac{\partial}{\partial\psi}\left(\frac{\sin\theta}{I\sin^2\theta}\frac{\partial}{\partial\psi} - \frac{\sin\theta\cos\theta}{I\sin^2\theta}\frac{\partial}{\partial\varphi'}\right) + \frac{\partial}{\partial\theta}\left(\frac{\sin\theta}{I}\frac{\partial}{\partial\theta}\right) \\ & + \frac{\partial}{\partial\varphi'}\left[\frac{\sin\theta\cos\theta}{I\sin^2\theta}\frac{\partial}{\partial\psi} + \left(\frac{\sin\theta}{I_z} + \frac{\sin\theta\cos^2\theta}{I\sin^2\theta}\right)\frac{\partial}{\partial\varphi'}\right] + \frac{\partial}{\partial\alpha}\left(\frac{\sin\theta}{rI_a}\frac{\partial}{\partial\alpha}\right)\Big\}, \\ = -\frac{\hbar^2}{2I}\Big\{ & \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi'} \right. \\ & \left. + \left(\frac{I}{I_z}\sin^2\theta + \cos^2\theta\right)\frac{\partial^2}{\partial\varphi'^2}\right] + \frac{I}{rI_a}\frac{\partial^2}{\partial\alpha^2}\Big\}. \end{aligned} \tag{H.12}$$

Now from the definitions $L^i_\chi \equiv \partial T/\partial\omega^i_\chi$, etc., we find by comparing (H.4), (H.6), and (H.12),

$$
\begin{aligned}
L_x^i &= \frac{\hbar}{i}\left[\sin\varphi'\frac{\partial}{\partial\theta} - \cos\varphi'\csc\theta\frac{\partial}{\partial\psi} + \cos\varphi'\cot\theta\frac{\partial}{\partial\varphi'}\right],\\
L_y^i &= \frac{\hbar}{i}\left[\cos\varphi'\frac{\partial}{\partial\theta} + \sin\varphi'\csc\theta\frac{\partial}{\partial\psi} - \sin\varphi'\cot\theta\frac{\partial}{\partial\varphi'}\right], \qquad \text{(H.13)}\\
L_z^i &= \frac{\hbar}{i}\frac{\partial}{\partial\varphi'},\\
L_\alpha^i &= \frac{\hbar}{i}\frac{\partial}{\partial\alpha}\,.
\end{aligned}
$$

APPENDIX I

THE INTEGRAL $S_{RR'}(abc;p)$

Given the generating function of the associate Laguerre polynomial

$$(1-t)^{-(\ell+1)} e^{-\frac{xt}{1-t}} = \sum_{n=0}^{\infty} \frac{t^n}{(n+\ell)!} L_n^{\ell}(x), \tag{I.1}$$

the integral

$$S_{RR'}(abc;p) = \int_0^{\infty} dx\, x^a e^{-(p+1)x} L_R^{a-b} L_{R'}^{a-c}, \tag{I.2}$$

can be evaluated. Consider

$$\begin{aligned}\Lambda &= \sum_{nm} \frac{t^n r^m}{(n+a-b)!\,(m+a-c)!} S_{nm}(abc;p), \\ &= (1-t)^{-(a-b+1)} (1-r)^{-(a-c+1)} \int_0^{\infty} dx\, x^a e^{-\Omega x}, \\ &= (1-t)^{-(a-b+1)} (1-r)^{-(a-c+1)} \frac{a!}{\Omega^{a+1}},\end{aligned} \tag{I.3}$$

where

$$\begin{aligned}\Omega &= p+1+\frac{t}{1-t}+\frac{r}{1-r}, \\ &= \left[\frac{p(1-t)(1-r)+1-rt}{(1-t)(1-r)}\right].\end{aligned} \tag{I.4}$$

Hence,

$$\Lambda = \frac{a!\,(1-t)^b (1-r)^c}{\left[1-\{rt-p(1-t)(1-r)\}\right]^{a+1}}. \tag{I.5}$$

By noting that

$$\left[1-\{rt-p(1-t)(1-r)\}\right]^{-(a+1)}=\sum_{\sigma}^{\infty}(-1)^{\sigma}\frac{(a+\sigma)!(1-t)^{\sigma}(1-r)^{\sigma}}{a!\,\sigma!}\left[p-\frac{rt}{(1-t)(1-r)}\right]^{\sigma}, \qquad \text{(I.6)}$$

and that

$$\left[p-\frac{rt}{(1-t)(1-r)}\right]^{\sigma}=\sum_{d}^{\sigma}(-1)^{d}\frac{\sigma!\,p^{\sigma-d}}{(\sigma-d)!\,d!}\left[\frac{rt}{(1-t)(1-r)}\right]^{d}, \qquad \text{(I.7)}$$

we can write

$$\Lambda=(1-t)^{b}(1-r)^{c}\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}(-1)^{\sigma+d}\frac{p^{\sigma-d}(a+\sigma)!}{(\sigma-d)!\,d!}(1-t)^{\sigma-d}(1-r)^{\sigma-d}(rt)^{d}. \qquad \text{(I.8)}$$

Due to the fact that b and c may be positive, negative, or zero we need to consider three cases separately.

<u>Case I</u>. b and c either positive or zero

Here we write

$$(1-t)^{b+\sigma-d}=\sum_{u}^{b+\sigma-d}(-1)^{u}\frac{(b+\sigma-d)!}{(b+\sigma-d-u)!\,u!}t^{u},$$

$$(1-r)^{c+\sigma-d}=\sum_{z}^{\sigma+\sigma-d}(-1)^{z}\frac{(c+\sigma-d)!}{(c+\sigma-d-z)!\,z!}r^{z}, \qquad \text{(I.9)}$$

so that

$$\Lambda=\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\sum_{u}^{b+\sigma-d}\sum_{z}^{c+\sigma-d}(-1)^{\sigma+d+u+z}$$

$$(\times)\frac{p^{\sigma-d}(a+\sigma)!(b+\sigma-d)!(c+\sigma-d)!\,t^{u+d}r^{z+d}}{(\sigma-d)!\,d!\,u!\,z!\,(b+\sigma-d-u)!\,(\sigma+c-d-z)!}. \qquad \text{(I.10)}$$

The value of $S_{RR'}(abc;p)$ is now given by the coefficient of $t^R r^{R'}$, so we set $u+d=R$, $z+d=R'$ thereby implying that $b+\sigma \geq R$, $c+\sigma \geq R'$. Therefore, we obtain

$$S_{RR'}(abc;p)=(-1)^{R+R'}(R'+a-c)!(R+a-b)!$$

$$^{(x)}\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\frac{(-1)^{\sigma+d}\,p^{\sigma-d}(a+\sigma)!(b+\sigma-d)!(c+\sigma-d)!}{d!(\sigma-d)!(R'-d)!(R-d)!(b+\sigma-R)!(c+\sigma-R')!}, \tag{I.11}$$

with $d<\min\begin{pmatrix}R+1\\R'+1\end{pmatrix}$ and $\sigma>\max\begin{pmatrix}R-b-1\\R'-c-1\end{pmatrix}$.

When $p=0$, the only non-vanishing term has $\sigma=d$, so that

$$S_{RR'}(abc;0)=(-1)^{R'+R}(R'+a-c)!(R+a-b)!c!b!$$

$$^{(x)}\sum_{\sigma}^{\infty}\frac{(a+\sigma)!}{\sigma!(R'-\sigma)!(R-\sigma)!(b+\sigma-R)!(c+\sigma-R')!}, \tag{I.12}$$

with

$$\max\begin{pmatrix}R-b-1\\R'-c-1\end{pmatrix}<\sigma<\min\begin{pmatrix}R'+1\\R+1\end{pmatrix}.$$

<u>Case II</u>. b negative but c positive or zero

Here we write

$$\Lambda=\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\frac{(-1)^{\sigma+d}(a+\sigma)!\,p^{\sigma-d}(1-t)^{\sigma-d}(1-r)^{c+\sigma-d}(rt)^{d}}{(c-d)!\,d!\,(1-t)^{|b|}}, \tag{I.13}$$

where we can expand

$$(1-t)^{-|b|}=\sum_{f}^{\infty}\frac{(|b|+f-1)!}{(|b|-1)!\,f!}t^{f}, \tag{I.14}$$

and again use (I.9) to find

$$\Lambda = \sum_{\sigma}^{\infty} \sum_{d}^{\sigma} \sum_{u}^{\sigma-d} \sum_{z}^{c+\sigma-d} \sum_{f}^{\infty} (-1)^{\sigma+d+u+z} \tag{I.15}$$

$$(\times) \frac{\rho^{\sigma-d}(a+\sigma)!(c+\sigma-d)!(|b|+f-1)!\, t^{u+d+f}\, r^{z+d}}{d!(|b|-1)!f!(c+\sigma-d-z)!z!(\sigma-d-u)!u!} \,.$$

The value of $S_{RR'}(a,-|b|,c;\rho)$ is again given by the coefficient of $t^R r^{R'}$, so we set

$$u+d+f=R, \quad z+d=R'$$

and find

$$S_{RR'}(a,-|b|,c;\rho)=(-1)^{R+R'}(R'+a-c)!(R+a-|b|)!$$

$$(\times)\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\sum_{f=R-\sigma}^{R-d}\frac{(-1)^{f+\sigma+d}\rho^{\sigma-d}(a+\sigma)!(c+\sigma-d)!(|b|+f-1)!}{d!f!(|b|-1)!(\sigma+f-R)!(R-f-d)!(R'-\sigma)!(c+\sigma-R')!}, \tag{I.16}$$

when $\rho=0$, the only non-vanishing term has $\sigma=d$ and $f=R-\sigma$, so that

$$S_{RR'}(a,-|b|,c;0)=(-1)^{R+R'}(R'+a-c)!(R+a-|b|)!\,c!$$

$$(\times)\sum_{\sigma}^{\infty}\frac{(-1)^{R-\sigma}(a+\sigma)!(|b|+R-\sigma-1)!}{\sigma!(R-\sigma)!(|b|-1)!(R'-\sigma)!(c+\sigma-R')!}\,. \tag{I.17}$$

Case III. b and c negative

Similar procedure leads to

$$S_{RR'}(a,-|b|,-|c|;\rho)=(-1)^{R+R'}(R'+a-|c|)!(R+a-|b|)!$$

$$(\times)\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\sum_{f=R-\sigma}^{R-d}\sum_{g=R'-\sigma}^{R'-d}\frac{(-1)^{f+g+\sigma+d}\rho^{\sigma-d}(a+\sigma)!(\sigma-d)!(|b|+f-1)!(|c|+g-1)!}{d!f!g!(|b|-1)!(|c|-1)!(\sigma+f-R)!(\sigma+g-R')!(R-f-d)!(R'-g-d)!} \tag{I.18}$$

and

$$S_{RR'}(a,-|b|,-|c|;0)=(R'+a-|c|)!(R+a-|b|)!$$

$$(\times)\sum_{\sigma}^{\infty}\frac{(a+\sigma)!(|b|-R-\sigma-1)!(|c|+R'-\sigma-1)!}{\sigma!(R-\sigma)!(R'-\sigma)!(|b|-1)!(|c|-1)!}. \tag{I.19}$$

REFERENCES

1. M. Born and J. R. Oppenheimer, "Zur Quantenthearie der Molekeln," Ann. d. Physik. 84, 457 (1927).

2. R. K. Osborn and E. H. Klevans, "Photon Transport Theory," Ann. of Phys. 15, 105 (1961).

3. A. Ziya Akcasu, "A Study of Line Shape With Heitler's Damping Theory," Technical Report 04836-1-T, The University of Michigan, April, 1963.

4. A. Ziya Akcasu, "Damping Theory and Its Application to the Interpretation of Slow Neutron Scattering Experiments," Technical Report 04836-2-T, The University of Michigan, July, 1963. See also, A. Z. Akcasu, Nuovo Cimento 38, 175 (1965).

5. E. Fermi, Ricera Sci. 7, 13 (1936); English translation, USAEC Rept. NP-2385.

6. G. Breit, Phys. Rev. 71, 215 (1947).
   G. Breit and P. Zilsel, Phys. Rev. 72, 516 (1947).
   P. Zilsel, B. Darling, and G. Breit, Phys. Rev. 72, 516 (1947).

7. B. A. Lippman, Phys. Rev. 79, 481 (1950).

8. J. P. Plummer and G. C. Summerfield, Phys. Rev. 131, 1153 (1963).

9. A. C. Zemach and R. J. Glauber, "Neutron Diffraction by Gases," Phys. Rev. 101, 129 (1956).

10. S. Yip, R. K. Osborn, and C. Kikuchi, "Neutron Acoustodynamics," Rept. IP-524, The University of Michigan, July, 1961.

11. A. C. Zemach and R. J. Glauber, "Dynamics of Neutron Scattering by Molecules," Phys. Rev. 101, 118 (1956).

12. L. Van Hove, "Correlation in Space and Time and Born Approximation Scattering in Systems of Interacting Particles," Phys. Rev. 95, 249 (1954. See also, G. Placzek, Phys. Rev. 86, 377 (1952) and G. C. Wick, Phys. Rev. 94, 1228 (1954).

13. J. P. Plummer, On Certain Common Approximations in Thermal Neutron Scattering, thesis, The University of Michigan, Ann Arbor, 1964.

14. S. Yip and M. Nelkin, "Application of a Kinetic Model to Time-Dependent Density Correlations in Fluids," Phys. Rev. 135A, 1241 (1964).

15. F. Zernike and J. Prins, Z. Physik. 41, 184 (1927).

16. M. Rosenbaum and P. F. Zweifel, "Comparison of 'Classical' and 'Quasi-Classical' Cross Sections for Some Simple Systems," Transactions of the International Conference on Neutron Thermalization, Brookhaven National Laboratory (1962). See also, R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, "Quasi-Classical Treatment of Neutron Scattering," Phys. Rev. 126, 1165 (1962).

17. M. Rosenbaum and P. F. Zweifel, Phys. Rev. 137, B271 (1965).

18. G. H. Vineyard, Phys. Rev. 110, 999 (1958).

19. P. A. Egelstaff, Nuc. Sci. and Eng. 12, 250 (1962). See also, G. C. Summerfield and P. F. Zweifel, Phys. Rev. 131, 1149 (1963).

20. P. A. Egelstaff and P. Schofield, Nuc. Sci. and Eng. 12, 260 (1962).

21. J. R. Triplett, J. U. Koppel, and David Naliboff, Trans. Am. Nuc. Soc. 8, 483 (1965).

22. P. Hutchinson and P. Schofield, ANL-7050 (TID-4500, 43d Ed.), 471 (1965).

23. A. Z. Akcasu and R. K. Osborn, "Inelastic Scattering of Neutrons," IAEA, Vienna (1965).

24. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.

25. R. G. Sachs and E. Teller, Phys. Rev. 60, 18 (1941).

26. T. J. Krieger and M. S. Nelkin, Phys. Rev. 106, 290 (1957).

27. H. C. Volkin, Phys. Rev. 113, 866 (1959) and 117, 1029 (1960).

28. A. Rahman, J. Nucl. Energy A13, 128 (1961).

29. G. W. Griffing, Phys. Rev. 124, 1489 (1961).

30. S. Brimberg, Thesis, Stockholm (1956).

31. J. Lovseth, Phys. Norv. (1962).

32. A. M. L. Messiah, Phys. Rev. 84, 204 (1951).

33. E. B. Wilson, Jr., Proc. Natl. Acad. Sci. U.S. 43, 816 (1957).

34. E. B. Wilson, Jr., "The Problem of Barriers to Internal Rotation in Molecules," Adv. in Chemical Physics, Vol. II, Interscience Publishers, Inc., New York, 1959.

35. R. Nasuhoglu and G. R. Ringo, J. Chem. Phys. 32, 476 (1960).

36. R. M. Brugger and J. E. Evans, "Inelastic Scattering of Neutrons in Solids and Liquids," IAEA, Vienna (1961).

37. D. H. Saunderson and V. S. Rainey, "Inelastic Scattering of Neutrons in Solids and Liquids," Vol. I, IAEA (1963), p. 413.

38. G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand Co., Inc., Princeton, N.J., 1945.

39. E. R. Andrew, Nuclear Magnetic Resonance, Cambridge University Press, New York, 1955.

40. H. S. Gutowsky and C. H. Holm, J. Chem. Phys. 25, 1228 (1956).

41. W. D. Phillips, J. Chem. Phys. 23, 1363 (1955).

42. E. O. Stejskal and H. S. Gutowsky, J. Chem. Phys. 28, 388 (1958).

43. E. B. Wilson, Jr., Chem. Rev. 27, 17 (1940).

44. K. S. Pitzer, Disc. of Faraday Soc. 10, 66 (1951).

45. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, 1955.

46. J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., Phys. Rev. Lett. 5, 507 (1960).

47. J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., Bull. Am. Phys. Soc. 6, 261 (1961).

48. J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., J. Chem. Phys. 35, 2265 (1961).

49. J. J. Rush, T. I. Taylor, W. W. Havens, Jr., and G. J. Safford, Bull. Am. Phys. Soc. 7, 24 (1962).

50. J. J. Rush, T. I. Taylor, and W. W. Havens, Jr., J. Chem. Phys. 37, 234 (1962).

51. J. J. Rush, T. I. Taylor, G. J. Safford, and W. W. Havens, Jr., Nuc. Sci. Eng. 14, 339 (1962).

52. J. J. Rush and T. I. Taylor, Bull. Am. Phys. Soc. 9, 413 (1964).

53. J. J. Rush, Bull. Am. Phys. Soc. 9, 623 (1964).

54. J. J. Rush and T. I. Taylor, "Inelastic Neutron Scattering," IAEA, Vienna (1965), p. 333.

55. J. A. Janik, J. M. Janik, J. Mellor, and H. Palevsky, J. Phys. Chem. Solids 25, 1091 (1964).

56. H. H. Nielsen, Rev. Mod. Phys. 23, 90 (1951) and Handbuch der Physik 37, 173 (1959).

57. C. Van Winter, Physica 20, 274 (1954).

58. Euler, Novi Comment. Petrop. 20, 189 (1776).

59. F. Reiche and H. Rademacher, Zeits. f. Physik 39, 444 (1926) and 41, 453 (1927). See also, R. Kronig and I. I. Rabi, Phys. Rev. 29, 262 (1927).

60. Frank and von Mises, Differentialgleichungen der Physik, Vol. I, 2d ed., Berlin (1930) p. 423.

61. P. M. Morse and H. Feshback, Methods of Theoretical Physics, Vol. I and II, McGraw-Hill, New York (1953).

62. E. P. Wigner, Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra, Academic Press, New York (1959).

63. M. E. Rose, Elementary Theory of Angular Momentum, Wiley, New York (1957).

64. M. Rotenberg, R. Bivins, N. Metropolis, J. K. Wooten, Jr., The 3-j and 6-j Symbols, Technology Press (MIT), Cambridge, Mass. (1959).

65. B. Czerlunczakiewicz and A. Kowalska, Acta Phys. Polon. 25, 141 (1964).

66. K. A. Strong, Y. D. Harker, and R. M. Brugger, J. Chem. Phys. 42, 1568 (1965).

67. G. W. Griffing, "Inelastic Scattering of Neutrons in Solids and Liquids," Vol. I, IAEA, Vienna (1963) p. 435.

68. G. Kosaly and G. Solt, Phys. Lett. 6, 51 (1963).

69. See J. A. Janik, "Inelastic Scattering of Neutrons," Vol. II, IAEA, Vienna (1965) p. 243.

70. R. W. Kilb, C. C. Lin, and E. B. Wilson, J. Chem. Phys. 26, 108 (1957).

71. R. W. Kilb and L. Pierce, J. Chem. Phys. 27, 108 (1957).

72. D. R. Herschbach, J. Chem. Phys. 31, 91 (1959).

73. S. Yip, The Scattering of Slow Neutrons by Polar Liquids, thesis, 1962, The University of Michigan.

74. B. L. Crawford, J. Chem. Phys. 8, 273 (1940).

75. H. H. Nielsen, Phys. Rev. 40, 445 (1932).

76. J. S. Kohler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).

77. D. G. Burkhard and D. M. Dennison, Phys. Rev. 84, 408 (1951).

78. K. T. Hecht and D. M. Dennison, J. Chem. Phys. 26, 31 (1957).

79. T. Itoh, J. Phys. Soc. Japan 11, 264 (1956).

80. E. V. Ivash and D. M. Dennison, J. Chem. Phys. 21, 1804 (1953).

81. K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. 10, 428 (1940).

82. E. B. Wilson, C. C. Lin, and D. R. Lide, J. Chem. Phys. 23, 136 (1955).

83. Tannenbaum, Johnson, Myers, Gwinn, J. Chem. Phys. 22, 949 (1954).

84. Tannenbaum, Myers, Gwinn, J. Chem. Phys. 25, 42 (1956).

85. D. G. Burkhard, Trans. Faraday Soc. 52, 1 (1956).

86. C. C. Lin and R. W. Kilb, J. Chem. Phys. 24, 631 (1956).

87. E. C. Kemble, Fundamental Principles of Quantum Mechanics, Dover Publications, Inc., New York, 1958, p. 394.

88. D. R. Herschback, "Tables for the Internal Rotation Problem," Dept. of Chemistry, Harvard University (1957). See also, J. Chem. Phys. 27, 975 and 1420 (1957), and J. Chem. Phys. 31, 91 (1959).

89. E. T. Whittaker and G. N. Watson, Modern Analysis.

90. G. H. Weiss and A. A. Maradudin, J. Math. Phys. 3, 771 (1962).

91. F. Bloch, Z. Physik 74, 295 (1932).

92. G. N. Watson, Bessel Functions, The Macmillan Company, New York (1948).

93. A. Morales and R. K. Osborn, "Inelastic Scattering of Neutrons By Solids and Liquids," IAEA, Vienna (1962), p. 251.

94. T. R. Hill, Statistical Mechanics, McGraw-Hill, New York (1956).

95. E. A. Straker, J. Chem. Phys. 42, 1111 (1965).

96. L. Pauling, Phys. Rev. 36, 430 (1930).

97. T. E. Stern, Proc. Roy. Soc. London, A130, 551 (1930).

98. R. Fowler, Proc. Roy. Soc. London, A149, 1 (1935); A151, 1 (1935).

99. H. H. Nielsen, J. Chem. Phys. 3, 189 (1935).

100. A. F. Devonshire, Proc. Roy. Soc. London, A153, 601 (1936).

101. Cundy, Proc. Roy. Soc. London, A164, 420 (1938).

102. P. Debye, Zeits. Physik 36, 100, 193 (1935).

103. L. Onsager, J. Am. Chem. Soc. 58, 1886 (1936).

104. J. Kirkwood, J. Chem. Phys. 7, 911 (1939).

105. J. Frenkel, Kinetic Theory of Liquids, Dover Publications, Inc., New York (1955).

106. S. Yip and R. K. Osborn, Phys. Rev. 130, 1860 (1963).

107. S. Yip and R. K. Osborn, Phys. Rev. 131, 2547 (1963).

108. W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. 42, 1419 (1920).

109. A. R. Ubbelohde, J. Chem. Phys. 46, 429 (1949).

110. D. J. Huges, et al, Phys. Rev. 119, 872 (1960).

111. K. Larsson, et al, "Inelastic Scattering of Neutrons in Solids and Liquids," IAEA, Vienna (1962).

112. K. C. Tuberfield, Proc. Phys. Soc. London, 80, 395 (1962).

113. A. Ookawa, J. Phys. Soc. Japan 15, 2191 (1960).

114. M. Rosenbaum, Tech. Report 03712-4-T, Office of Research Administration, University of Michigan, Ann Arbor (1963).

115. A. Rahman, K. S. Singwi, and A. Sjolander, Phys. Rev. 126, 997 (1962).

116. A. L. McClellan, Tables of Experimental Dipole Moments, W. H. Freeman and Co., San Francisco (1963).

117. J. A. Janik, Acta Phys. Polon. 13, 167 (1954).

118. F. Borowski and H. Rzany, Nukleonika 10, 201 (1965).

119. M. Falk and E. Whalley, J. Chem. Phys. 34, 1554 (1961).

120. T. Titani, Bull. Chem. Soc. Japan 8, 255 (1933).

121. W. H. Zachariasen, J. Chem. Phys. 3, 158 (1935).

122. G. E. Bacon, Neutron Diffraction, Clarendon Press, Oxford (1955).

123. K. E. Larsson, "Inelastic Scattering of Neutrons," Vol. II, IAEA, Vienna (1965) p. 3.

124. H. Boutin, G. Safford, and V. Brajovic, Bull. Am. Phys. Soc. 7, 500 (1962).

125. H. Boutin and G. J. Safford, "Inelastic Scattering of Neutrons," Vol. II, IAEA, Vienna (1965) p. 393.

126. E. Teller and B. Topley, J. Chem. Soc., 885 (1935).

127. L. J. B. LaCoste, Phys. Rev. 46, 718 (1934).

128. K. S. Singwi and G. Feldmann, "Inelastic Scattering of Neutrons," Vol. II, IAEA, Vienna (1965) p. 85. See also, K. S. Singwi, Phys. Rev. 136, A969 (1964) and Physica 31, 1257 (1965).

129. W. Kohn, Phys. Rev. Letters 2, 393 (1959).

130. B. N. Brockhouse, K. R. Rao, and A. D. B. Woods, Phys. Rev. Letters 7, 93 (1961).

131. H. L. McMurray, Nuc. Sci. and Eng. 15, 429 (1963), and 15, 438 (1963).

132. P. A. Egelstaff, "Inelastic Scattering of Neutrons," Vol. II, IAEA, Vienna (1965) p. 553.

133. R. M. Thaler, "International Conference on Nuclear Physics With Reactor Neutrons," ANL-6797 (1963) p. 2.

134. P. Stein, et al, Phys. Rev. Letters 16, 592 (1966).

135. M. Blume, "Symposium on Inelastic Scattering of Neutrons by Condensed Systems," BNL-940 (C-45), (1965) p. 1.

136. R. Fowler and E. Guggenheim, Statistical Thermodynamics, Cambridge University Press, 1949.

137. I. Z. Fisher, Statistical Theory of Liquids, University of Chicago Press, Chicago (1964).

138. T. J. Hughel, Ed., Liquids: Structure, Properties, Solid Interactions, Elsevier Publishing Co., New York (1965).

139. Lucretius, The Nature of Things, J. M. Dent and Sons, New York.

140. L. B. Loeb, The Kinetic Theory of Gases, McGraw-Hill, New York (1927).

141. J. Perrin, Atoms, Constable and Co., London (1920).

142. J. A. Barker, Lattice Theories of the Liquid State, The MacMillan Co., New York (1963).

143. S. A. Rice and P. Gray, Statistical Mechanics of Simple Liquids, Academic Press, New York (1966).

144. J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. A163, 53 (1937) and A165, 1 (1938).

145. J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. A169, 317 (1939) and A170, 469 (1939). Also see, Proc. Roy. Soc. A174, 102 (1940) and A178, 401 (1941).

146. H. Eyring, Statistical Mechanics and Dynamics, Wiley and Sons, New York (1964).

147. J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

148. M. Born and H. S. Green, A General Kinetic Theory of Liquids, Cambridge University Press, 1949. See also, H. S. Green, Molecular Theory of Fluids, North Holland Publishing Co., Amsterdam (1952).

149. W. W. Wood and J. D. Jacobson, J. Chem. Phys. 27, 1207 (1957).

150. L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1965).

151. P. G. de Gennes, Physica 25, 825 (1959).

152. K. S. Singwi and A. Sjolander, Phys. Rev. 119, 863 (1960).

153. V. S. Oskotskii, Soviet Phys.-Sol. State 5, 789 (1963).

154. P. Schofield, Fluctuation, Relaxation, and Resonance in Magnetic Systems, Scottish University, Edinburgh (1962) p. 207.

155. P. A. Egelstaff and P. Schofield, Nucl. Sci. Engr. 12, 260 (1962).

156. G. W. Griffing, Symposium on Inelastic Scattering of Neutrons by Condensed Systems, BNL-940 (C-45), (1966) p. 149.

157. P. Debye, Ann. Physik 46, 809 (1915).

158. P. Ehrenfest, Koninkl. Ned. Akad. Wetenschapp. Proc. 17, 1184 (1915).

159. P. Debye and P. Scherrer, Nachr. Ges. Wiss. Gottingen, 1 (1916).

160. W. H. Kelsom and J. De Smedt, Koninkl. Ned. Akad. Wetenschapp. Proc. 25, 118 (1922); 26, 112 (1923).

161. P. Debye, Z. Physik 28, 135 (1927).

162. P. Debye and H. Menke, Z. Physik 31, 797 (1930).

163. N. S. Gingrich, Rev. Mod. Phys. 15, 90 (1943).

164. K. Furukawa, Rept. Prog. Phys. 25, 395 (1962).

165. R. F. Kruh, Chem. Rev. 62, 319 (1962).

166. H. H. Paalman and C. J. Pings, Rev. Mod. Phys. 35, 389 (1963).

167. W. M. Elsasser, C. R. Acad. Sci. Paris 202, 1029 (1936).

168. H. Halban and P. Preiswerk, C. R. Acad. Sci. Paris 203, 73 (1936).

169. D. P. Mitchell and P. N. Powers, Phys. Rev. 50, 486 (1936).

170. O. Chamberlain, Phys. Rev. 77, 305 (1950).

171. P. C. Sharrah and G. P. Smith, J. Chem. Phys. 21, 228 (1953).

172. D. G. Henshaw, D. G. Hurst, and N. K. Pope, Phys. Rev. 92, 1229 (1953).

173. D. G. Henshaw, Phys. Rev. 105, 976 (1957).

174. R. Rahman, J. Chem. Phys. 42, 3540 (1965).

175. W. A. Schlup, Symposium on Inelastic Scattering of Neutrons by Condensed Systems, BNL-940 (C-45), (1966) p. 183.

176. R. M. Mazo and A. C. Zemach, Phys. Rev. 109, 1564 (1958).

177. A. Paskin and A. Rahman, Phys. Phys. Rev. Letters 16, 300 (1966).

178. H. Goldstein, Classical Mechanics, Addison-Wesley Publishing Co., Reading, Mass. (1959).

179. H. Margenau and G. Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand, New York (1957).

180. S. C. Wang, Phys. Rev. 34, 243 (1929).