THE SCATTERING OF SLOW NEUTRONS BY POLAR LIQUIDS

by

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ABSTRACT

A quasi-crystalline model of polar liquids for the analysis of slow-neutron scattering is proposed. Effects of the macroscopic medium are considered in terms of specific potentials which hinder molecular translations and rotations. By smearing the neighboring molecules over a spherical distribution and choosing a two-particle interaction which includes dipole-dipole forces an effective potential for the center-of-mass degrees of freedom is derived. A sufficient condition for the parabolic approximation to this potential is established. Hindrance in the rotational motion is treated by means of a coupling between the permanent electric dipole moment of the molecule and a local electric field which represents orientation-dependent effects of intermolecular forces. Under the condition of strong coupling this hindering potential leads to useful wave functions for symmetric and linear molecules which describe free as well as hindered rotations. On the basis of the present treatment of molecular translations and rotations the energy and angular differential scattering cross section is calculated without introducing further approximations. Particularly simple expressions are obtained when free-rotation energies are ignored. Energy distributions of neutrons scattered by hydrogen chloride and water are calculated. It is shown that hindered rotation effects are experimentally observable whereas the structure associated with hindered translations can be observed only by means of high-resolution measurements. The present results provide a suitable basis for systematic studies of medium effects in polar liquids by inelastic slow-neutron scattering. Specific experiments are suggested.

CHAPTER I

INTRODUCTION

In recent years considerable attention has been directed toward the use of inelastic scattering of slow ($\epsilon \sim 10^{-3} - 10^{-2}$ ev) neutrons for the study of atomic motions in macroscopic systems. Of the various modes of molecular motions, translation of the center-of-mass and rotation are of particular interest because of their more sensitive dependence upon the physical state of the medium. The characteristic energies associated with these motions are of the order of 10^{-3}-10^{-2}ev, so in the event of an inelastic collision with a neutron the energy transfer is of the same order as the incident neutron energy. The energy spectrum of the scattered neutrons therefore provides a means with which the details of molecular translations and rotations, and the effects on these motions due to surroundings in a liquid or a crystal, can be directly examined. In this respect, slow neutrons are very suitable microscopic probes for the investigation of intermolecular forces.

The general problem of low-energy neutron scattering by free molecules has been considered by Zemach and Glauber[1] in treating those systems which can be characterized by the degrees of freedom appropriate to gas molecules. Krieger and Nelkin,[2] in a somewhat different approach, used the Sachs-Teller mass tensor approximation[3] to describe the combined effects of translations and rotation. Both methods[2,4] give results for gaseous methane in good agreement with measurements.[5]

In crystals the translational degrees of freedom can be appropriately characterized by a system of oscillators (if diffusion in crystals is ignored) according to a dynamical description such as that of Debye or Born-Von Kármán.[6] The first general treatment of neutron scattering by crystals was given by Weinstock;[7] subsequently the theory has been refined and valuable information about interatomic forces in crystals, namely, frequency distribution and dispersion relations, have been obtained by means of neutron diffraction studies.[8,9]

The analysis of neutron scattering by liquids is considerably more difficult since the dynamics of molecular translations and rotations are much more complicated. In the absence of detailed knowledge of intermolecular forces it has become necessary, in cases where a specific model is used to interpret measurements, to introduce greatly simplified descriptions. Commonly either a gas-like or crystal-like description is employed for the translational degrees of freedom. A number of slow-neutron experiments using liquid tin,[10] ammonium halides,[11] and water[12-14] have been reported where the results tend to support the point of view that liquids behave much like disordered crystals with short range ordering and that the molecules spend appreciable amount of time in a localized region before undergoing diffusion. The energy distributions of neutrons scattered by water at very low energies[12,13] showed considerable structure in the region of small energy transfer and this structure is regarded as direct evidence of hindered translational motions.

Morales[15] has studied hindered translations in normal liquids and has found that an Einstein-crystal model of liquid lead leads to energy broadenings in better agreement with observed values[16] than those predicted by a continuous diffusion model proposed by Vineyard.[17] Singwi and Sjölander[18] have shown that the previously mentioned structure in the water results[12] can be calculated by treating the liquid as a Debye crystal. They have also suggested a model in which each molecule intermittently undergoes oscillations and diffusions. On the basis of an extensive series of measurements Larsson and coworkers[13] concluded that on the average the water molecule performs about ten oscillations during a period of $\sim 2 \times 10^{-12}$ sec before diffusing a distance of at least 1.5Å. Since the time interval in which a slow neutron ($v \sim 10^5$ cm/sec) is in the immediate vicinity of a molecule is approximately 10^{-13} sec, then the supposition that dominant aspects of translational motions are crystal-like seems reasonable, at least in so far as slow-neutron scattering is concerned. Although quasi-crystalline models have been employed with some success in correlating with experimental data, the only attempt to justify such descriptions on theoretical basis has been made by Morales in the case of normal liquids.

In addition to translations, molecular rotations in liquids can also become hindered as a result of intermolecular interactions. The phenomenon of hindered rotation has been observed in water[12-14] and in ammonium halides[11] using the neutron technique, and also in Raman spectra[19] and infrared absorption[20] studies. In early papers, Pauling[21] has considered the rotational motion in crystals in connection with its influence on the dielectric constant, and Magat[22] has carried out an electrostatic calculation to determine the amount of energy a water molecule must acquire in order to have complete freedom of rotation in the potential field of four nearest neighbors. Aside from these considerations the study of hindered rotation in liquids and crystals has received little theoretical attention. Thus far, the effect of this type of motion upon neutron scattering has been treated only recently by Nelkin,[23] who, in constructing a model for water, assumed that the hindered molecular rotations can be replaced by a single mode of torsional oscillation. Nelkin's approach is phenomenological, and the model, although providing an adequate basis for calculations of neutron thermalization in nuclear reactors, does not lead to much physical insight as to the nature of intermolecular forces in liquids.

In the present work we propose a dynamical model for polar liquids for the analysis of slow-neutron scattering. The atomic motions are considered in terms of molecular translations, rotations, and internuclear vibrations. The model consists of descriptions, derived in a systematic and consistent approach, of translations and rotations in the presence of appreciable intermolecular interactions.

The method used by Morales in treating normal liquids is extended in order to study molecular translations in polar liquids where noncentral forces arising from dipole-dipole couplings are taken into account. For those liquids where the existence of short range ordering can be expected, an averaged, effective single-particle potential for the center-of-mass degrees of freedom is derived. This potential provides, in principle, at least a qualitative representation of the interactions generated by neighboring molecules in the liquid. To the extent that a certain condition can be satisfied by the parameters characterizing the two-particle potential employed, some theoretical justification for the use of oscillator models in treating translational motions is obtained.

A description of the rotational motions of polar molecules is proposed in which the permanent electric dipole moment of the molecule is coupled to a local electric field which represents the orientation-dependent effects produced by the ordered near neighbors. In the case of strong coupling, physically meaningful solutions for symmetric and linear molecules are obtained. The model treats free as well as hindered rotations because in this instance the potential contains only one angular variable.

On the basis of the proposed model an energy and angular differential cross section is calculated. New formulae for the scattering by rotational degrees of freedom are obtained. The results of the present investigation are considerably less empirical than Nelkin's treatment since the molecular rotational degrees of freedom, the polar nature of the molecule, and internuclear separations appear explicitly in the expression for the intensity of the scattering. Moreover, the approach allows the magnitudes of the energy transfer to be directly estimated in terms of the dipole moment of the molecule, the moment of inertia, and the crystalline electric field in the corresponding solid phase. Numerical computations are presented in which the calculated energy distributions are compared with the available water data and future scattering measurements are suggested.

In Chapter II the formalism of Zemach and Glauber is derived and a general expression for the energy and angular differential cross section is obtained.* The single-particle model is then adopted in which couplings between translation, rotation, and vibration are ignored so that these motions can be studied separately. Hindered molecular translation is treated in Chapter III in terms of a potential obtained by appropriate position and orientation averages of the two-particle Stockmayer potential. A sufficient condition for an Einstein-crystal approximation is established, and the cross section for a system of oscillators is calculated. The dynamics of free molecular rotation are reviewed in Chapter IV where the known symmetry properties of the wave functions are utilized in computing the cross sections for asymmetric, symmetric and linear molecules rigorously. A rotator model of hindered rotation is proposed in Chapter V. A formal solution of the molecular problem is first discussed, then strong-field solutions for symmetric and linear molecules are obtained and used in cross section calculations. Effects

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*Van Hove[24] has discussed neutron scattering in terms of space and time correlation functions. This approach is quite general and has been extensively used by Egelstaff[25] and others.[26] Inasmuch as specific models are proposed and employed in the present work there is no advantage to consider Van Hove's approach.

of free and hindered motions are examined, and using the method of mass-ratio expansion[1] the angular differential cross section in the limit of high incident energy is derived. Numerical computations for hydrogen chloride and water are discussed in Chapter VI. In the case of water, the molecule is approximated by a diatomic molecule of equal mass and having the same dipole moment. Concluding remarks regarding the present model are given in Chapter VII where specific scattering experiments are also suggested.

CHAPTER II

GENERAL FORMULATION OF NEUTRON SCATTERING BY MACROSCOPIC SYSTEMS

In this section a general description of neutron scattering by molecules in an arbitrary macroscopic system is developed. The formalism is suitable for the analysis of low-energy inelastic scattering by liquids on the basis of specific dynamical models. In order to calculate the effects characteristic of atomic motions in the liquid state an independent-particle model is adopted in which molecular translations, rotations, and vibrations are approximated by independent motions. Each motion can then be treated separately.

We consider an idealized experiment to illustrate the type of measurements with which subsequent calculations are to be correlated. A beam of monoenergetic neutrons impinges upon a scattering system as shown in Fig. 1, and collisions between the neutrons and target molecules result in some of the neutrons being deflected from the original path with energies greater or less than that before scattering. By counting neutrons of a given energy scattered in a given direction, an energy distribution is obtained. If neutrons of all energies are counted for a given direction, then by repeating this measurement at different scattering angles an angular distribution is obtained. Finally, if all scattered neutrons are counted regardless of their directions or energies then the measurement is said to be a total scattering measurement and the result depends only upon the incident energy. We observe that of the three types of

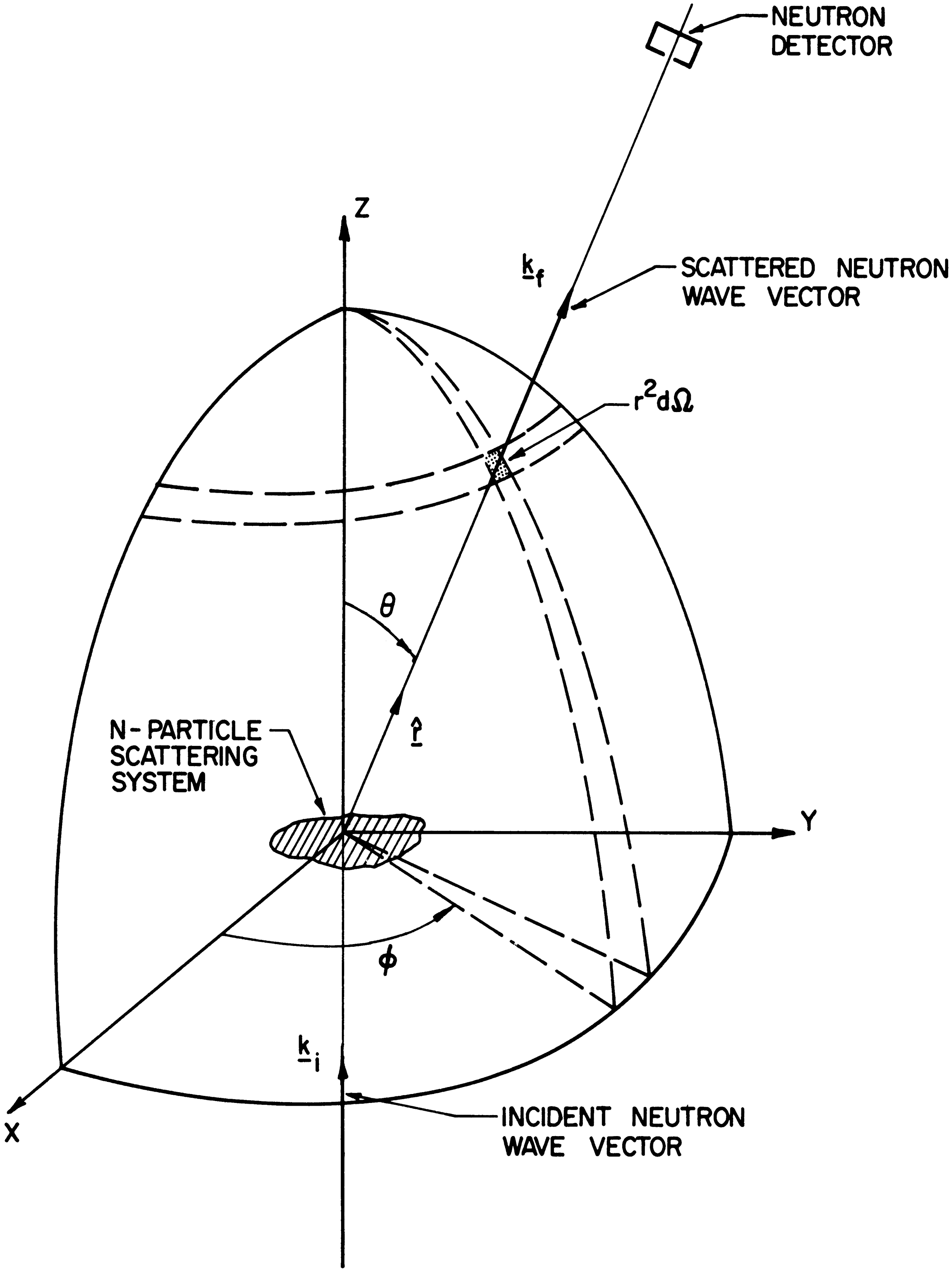

Fig. 1. Schematic diagram of neutron scattering experiment.

measurement, the energy distribution experiment is the most fundamental and should provide maximum information about the scattering process, and that with respect to it the other two are integral measurements. The scattering event under consideration is a single collision process, and the resolution of the neutron detector shown in Fig. 1 is infinitely sharp. In practice, however, the thickness of the sample is dictated by multiple scattering and effects of finite resolution, which is inherent in any energy measurement device, must be taken into account in specific applications.

The energy distribution measurement can be analyzed in terms of a fundamental quantity which characterizes the interaction, the probability that an incident neutron with initial energy ϵ_i will be scattered into direction $\underline{\Omega}$ with final energy ϵ_f. When appropriately normalized to unit scatterer, this probability becomes a differential cross section $\sigma(\epsilon_i,\underline{\Omega},\epsilon_f)$ which, we emphasize, is a distribution in final neutron energy and direction.

In order to derive an expression for $\sigma(\epsilon_i,\underline{\Omega},\epsilon_f)$ we return to the idealized experiment of Fig. 1. The number of neutrons scattered into an element of solid angle $d\Omega$ about $\underline{\Omega}$ (denoted by $\hat{\underline{r}}$) per unit incident neutron with energy ϵ_i and per unit scatterer is

$$\sigma(\epsilon_i,\underline{\Omega})\,d\Omega = \frac{r^2(\hat{\underline{r}}\cdot\underline{J})}{N(\hat{\underline{z}}\cdot\underline{J}_i)}\,d\Omega \qquad (2.1)$$

where $\underline{J}_i$ and $\underline{J}$ are initial and final neutron currents and N is the total number of scattering centers. From the well-known relation

$$\underline{J} = \left(\frac{i\hbar}{2m}\right)\left[(\underline{\nabla}\psi)^{\dagger}\psi - \psi^{\dagger}(\underline{\nabla}\psi)\right]. \tag{2.2}$$

where $\hbar = \frac{h}{2\pi}$, h being the Planck's constant, m is the neutron mass, and ψ is the neutron wave function, the cross section can therefore be calculated once the initial and final neutron wave functions are determined. The initial wave function may be taken as a plane wave with wave vector $\underline{k}_i$. The final neutron wave function necessarily depends upon the particular scattering process involved, and can be derived from the appropriate stationary Schrödinger equation,

$$H\Psi = E\Psi, \tag{2.3}$$

where E is the total energy of the system, molecules plus neutron, whose wave function is Ψ. The appropriate Hamiltonian is

$$H = \frac{P^2}{2m} + H_S + V, \tag{2.4}$$

where $\frac{P^2}{2m}$ is the kinetic energy of the neutron, H_S the Hamiltonian of the scattering system, and V the neutron-nuclear interaction potential.

The Hamiltonian H_S represents only the various molecular energies of the scattering system. Because in the experiments under consideration the neutron energies are much too low to excite any electronic levels, and also electron scattering is negligible, the electronic energies are of no interest and have been separated by means of the Born and Oppenheimer approximation.[27] It is expected that given H_S, there exists a complete, orthonormal set of functions $\{\Phi_n\}$ which satisfy the equation, $H_S\Phi_n = E_n\Phi_n$, where E_n is the energy eigenvalue of the system associated with the nth eigenstate. Then we can consider the expansion

$$\Psi(\underline{r},\underline{R}) = \sum_n \psi_n(\underline{r}) \Phi_n(\underline{R}), \tag{2.5}$$

where $\underline{r}$ represents neutron position and $R = \{R_1, R_2, \ldots, R_N\}$ represents the set of $3N$ coordinates of a system containing N particles. The function ψ_n is seen to be that neutron state which corresponds to the nth state of the system. Inserting the above expansion in (2.3) we obtain

$$(\nabla^2 + k_n^2)\psi_n = \frac{2m}{\hbar^2} \sum_{n'} \langle n|V|n'\rangle \psi_{n'}, \tag{2.6}$$

where

$$\langle n|V|n'\rangle = \int d^3R\, \Phi_n^* V \Phi_{n'}$$

$$k_n^2 = \frac{2m}{\hbar^2} \epsilon_n \;;\quad \epsilon_n = E - E_n$$

Equation (2.6) represents a set of integro-differential equations and is conveniently converted to a set of integral equations. If we define a Green's function $G_n(\underline{r},\underline{r}')$ by

$$(\nabla^2 + k_n^2) G_n(\underline{r},\underline{r}') = -\delta(\underline{r}-\underline{r}'), \tag{2.7}$$

then because (2.6) is a linear equation,

$$\psi_n(\underline{r}) = \psi_n^0(\underline{r}) - \frac{2m}{\hbar^2} \sum_{n'} \int d^3r'\, G_n(\underline{r},\underline{r}') \langle n|V|n'\rangle \psi_{n'}(\underline{r}'), \tag{2.8}$$

where ψ_n^0 satisfies

$$(\nabla^2 + k_n^2)\psi_n^0(\underline{r}) = 0. \tag{2.9}$$

Physically, if there were no interaction between the neutron and system we would expect Ψ to be just the product of incident neutron and initial system wave functions. Hence,

$$\psi_n^0(\underline{r}) = \delta_{nn_0}\, e^{i\underline{k}_i\cdot\underline{r}} , \qquad (2.10)$$

where n_0 denotes the initial state of the scattering system. The solution of (2.7) is[28]

$$G_n(\underline{r},\underline{r}') = \frac{e^{ik_n|\underline{r}-\underline{r}'|}}{4\pi|\underline{r}-\underline{r}'|} \simeq \frac{e^{ik_n r}}{4\pi r}\, e^{-i\underline{k}_n\cdot\underline{r}'} + \theta(r^{-2}), \qquad (2.11)$$

where terms of order r^{-2} and higher can be ignored as the region of detection is such that $\frac{r}{r'} \gg 1$. In fact, in the limit $\frac{r}{r'}\to\infty$ contribution to neutron current from higher-order terms vanish identically. An approximate solution to the integral equation (2.8), according to the "first Born approximation," is obtained by iterating once,

$$\psi_n(\underline{r}) \simeq \delta_{nn_0}\, e^{i\underline{k}_i\cdot\underline{r}} + f_{nn_0}(\underline{\Omega})\,\frac{e^{ik_n r}}{r} . \qquad (2.12)$$

The first term in (2.12) represents the unscattered incident beam and the second term can be interpreted as the spherically outgoing scattered wave whose amplitude is

$$f_{nn_0}(\underline{\Omega}) = -\frac{m}{2\pi\hbar}\int d\underline{r}'^3\, e^{i(\underline{k}_i-\underline{k}_n)\cdot\underline{r}'} \langle n|V|n_0\rangle . \qquad (2.13)$$

Using the results just derived we arrive at a formal expression for the differential cross section of (2.1),

$$\sigma(\epsilon_i,\underline{\Omega})d\Omega = N^{-1}\sum_{n,n_0} P_{n_0}(k_n/k_i)\,|f_{nn_0}|^2\, d\Omega, \qquad (2.14)$$

where we average over initial system states and sum over all possible final system states because they cannot be observed. The probability that the system is in initial state n_0 is denoted by P_{n_0}, which becomes a Kronecker delta should the scattering system be initially prepared.

For each collision process in which the scattering system undergoes a transition from state n_0 to state n, the associated condition of energy conservation,

$$E_n + \epsilon_n = E_{n_0} + \epsilon_{n_0} \tag{2.15}$$

must be satisfied. It will be convenient to incorporate this statement into the cross section.[29] By defining

$$\int_{\epsilon_f} \sigma(\epsilon_i, \Omega, \epsilon_f)\, d\Omega\, d\epsilon_f = \sigma(\epsilon_i, \Omega)\, d\Omega \tag{2.16}$$

and noting the integral representation of the Dirac delta function,

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

we obtain an expression for the energy and angular differential cross section,*

$$\sigma(\epsilon_i, \Omega, \epsilon_f)\, d\Omega\, d\epsilon_f = \frac{k_f\, d\Omega\, d\epsilon_f}{2\pi N k_i} \int dt\, e^{-it(\epsilon_f - \epsilon_i)} \\ (\times) \sum_{n n_0} P_{n_0} |f_{n n_0}|^2 e^{-it(E_n - E_{n_0})}, \tag{2.17}$$

where on account of the delta function k_n and ϵ_n can be written as k_f

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*In the present notation the variable t has the unit of reciprocal energy, that is to say, $t = \tau/\hbar$ where τ has the unit of time.

and ϵ_f; this is to avoid confusion and to indicate that the scattered neutron energy is an observed quantity. The manipulation also conveniently removes the factor $\frac{k_n}{k_i}$ from the summand.

It is noted that the amplitude of the scattered wave (2.13) contains the neutron-nuclear interaction potential V which has yet to be specified. For neutron energy sufficiently low $(\epsilon_i \lesssim eV)$ such that its wavelength is large compared to the range of nuclear forces, neutron-nuclear collisions can be represented quite accurately as a "localized impact" for which the interaction potential may be taken as the "Fermi pseudopotential,"*[30]

$$V = \frac{2\pi\hbar^2}{m} \sum_{l\alpha} a_{l\alpha} \delta(\underline{r} - \underline{r}_{l\alpha}), \tag{2.18}$$

where $a_{l\alpha}$ is the scattering length of α-th nucleus in the l-th molecule, whose position is $\underline{r}_{l\alpha}$, and summation is over all nuclei and molecules in the system. This particular form of the potential is so chosen that when used with the "first Born approximation" the correct total scattering cross section for a free atom is guaranteed in the high-energy limit $(\epsilon \gtrsim eV)$; i.e., $\sigma \rightarrow 4\pi a_f^2$, where a_f is the experimentally determined free-atom scattering length and is related to the so-called bound-atom scattering length by $a_b = \frac{m+M}{M} a_f$, M being the mass of the scatterer. With this choice of the potential the scattered amplitude takes the form

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*The use of pseudopotential is appropriate so long as the incident neutron is in the energy range for which nuclear scattering is isotropic in the center-of-mass coordinate system and independent of neutron energy.

$$f_{nn_0} = -\sum_{l\alpha} \langle n | a_{l\alpha} e^{-i\underline{K}\cdot\underline{r}_{l\alpha}} | n_0 \rangle , \tag{2.19}$$

where $\underline{K} = \underline{k}_i - \underline{k}_f$ is the neutron momentum transfer. The differential cross section thus becomes

$$\sigma(\epsilon_i, \Omega, \epsilon_f) = \frac{k_f}{2\pi N k_i} \int dt \, e^{-i\epsilon t} \sum_{\substack{ll' \\ \alpha\alpha'}} \langle \chi'_{\substack{ll' \\ \alpha\alpha'}} \rangle_T , \tag{2.20}$$

where $\langle \chi'_{\substack{ll' \\ \alpha\alpha'}} \rangle_T = \sum_n P_n \langle n | a_{l\alpha} a_{l'\alpha'} e^{itH_s} e^{i\underline{K}\cdot\underline{r}_{l\alpha}} e^{-itH_s} e^{-i\underline{K}\cdot\underline{r}_{l'\alpha'}} | n \rangle$

$$= \langle a_{l\alpha} a_{l'\alpha'} e^{itH_s} e^{i\underline{K}\cdot\underline{r}_{l\alpha}} e^{-itH_s} e^{-i\underline{K}\cdot\underline{r}_{l'\alpha'}} \rangle_T \tag{2.21}$$

and where $\epsilon = \epsilon_f - \epsilon_i$. In arriving at (2.21) we have used the closure property of the wave function to perform the sum over final states. The subscript T is used to denote the average of the expectation value of the indicated operator in a given initial eigenstate n (previously n_0) over all initial states; because the scattering system is usually taken to be in thermodynamic equilibrium the quantity $\langle \; \rangle_T$ is often called a thermal average. Expressions (2.20) and (2.21) represent the basic equations used by Zemach and Glauber[1] in treating neutron scattering by gases. Since the Hamiltonian for the scattering system has not yet been specified these expressions can be applied to crystals and liquids as well.

We have purposely placed $a_{l\alpha} a_{l'\alpha'}$ between the initial system wave functions. The reason for this is that (2.21) can be generalized to include spin effects which we have not considered thus far and which can be taken into account by introducing a spin-dependent expression for the scattering length,

$$a_{l\alpha} = A_{l\alpha} + B_{l\alpha}(\underline{s}\cdot\underline{S}_{l\alpha}), \tag{2.22}$$

where $\underline{s}$ and $\underline{S}$ are respectively the neutron and nuclear spins, and A, B are nuclear constants to be determined by experiment. The necessary modification in (2.21) merely requires that the thermal average to include the matrix elements of spin-dependent factors. The system eigenfunction now appears as $\Phi_n \chi_m$, where nuclear spin function χ_m is a column vector specified by m, the projection of the nuclear spin along the z axis. Separation of spin and coordinate dependences is not always allowed; however, it has been shown[4] that spin correlation effects may be neglected for all but the lightest diatomic molecules containing like nuclei (e.g., H_2 and D_2) at very low temperatures. The thermal average (2.21) becomes

$$\langle \chi'_{\substack{ll'\\ \alpha\alpha'}} \rangle_T = \sum_s P_s \langle s| a_{l\alpha} a_{l'\alpha'} |s\rangle_T \langle e^{itH_s} e^{i\underline{\kappa}\cdot\underline{r}_{l\alpha}} e^{-itH_s} e^{-i\underline{\kappa}\cdot\underline{r}_{l'\alpha'}} \rangle_T , \tag{2.23}$$

where s specifies the neutron spin function represented by a two-component column vector.

The spin thermal average in (2.23) can be readily performed by noting the following:

$$\sum_s P_s \langle s| \underline{s}\cdot\underline{S}_{l\alpha} |s\rangle_T = 0 , \tag{2.24}$$

$$\sum_s P_s \langle s| (\underline{s}\cdot\underline{S}_{l\alpha})(\underline{s}\cdot\underline{S}_{l'\alpha'}) |s\rangle_T = \frac{1}{4} S_{l\alpha}(S_{l\alpha}+1)\,\delta_{ll'}\,\delta_{\alpha\alpha'} . \tag{2.25}$$

Hence

$$\sum_S P_S \langle S|a_{l\alpha}a_{l'\alpha'}|S\rangle_T = A_{l\alpha}A_{l'\alpha'} + \frac{1}{4}B^2_{l\alpha}S_{l\alpha}(S_{l\alpha}+1)\delta_{ll'}\delta_{\alpha\alpha'} . \qquad (2.26)$$

This result leads to a convenient and meaningful separation of the cross section into various contributions,

$$\sigma(\epsilon_i, \Omega, \epsilon_f) = \frac{k_f}{2\pi N k_i}\int dt\, e^{-i\epsilon t}\Big\{\sum_{l\alpha} D^2_{l\alpha}\langle \chi_{\substack{ll\\ \alpha\alpha}}\rangle_T$$
$$+ \sum_{l}\sum_{\alpha\alpha'}{}' A_{l\alpha}A_{l\alpha'}\langle \chi_{\substack{ll\\ \alpha\alpha'}}\rangle_T + \sum_{ll'}{}'\sum_{\alpha\alpha'} A_{l\alpha}A_{l'\alpha'}\langle \chi_{\substack{ll'\\ \alpha\alpha'}}\rangle_T\Big\} , \qquad (2.27)$$

where the prime over the summation indicates that terms for which the two indices being equal are to be omitted. In this notation,

$D^2_{l\alpha} = A^2_{l\alpha} + B^2_{l\alpha}S_{l\alpha}(S_{l\alpha}+1)/4$ and

$$\langle \chi_{\substack{ll'\\ \alpha\alpha'}}\rangle_T = \langle e^{itH_s} e^{i\kappa\cdot r_{l\alpha}} e^{-itH_s} e^{-i\kappa\cdot r_{l'\alpha'}}\rangle_T . \qquad (2.28)$$

The three terms in (2.27) represent contributions due to direct, "inner" (interference within the same molecule) and "outer" (interference from different molecules) scatterings. The nuclear constants A and $B[S(S+1)]^{1/2}/2$ are conventionally known as the coherent and incoherent scattering amplitudes respectively. They are related to the "parallel" and "anti-parallel" (total spin = $S \pm 1/2$ respectively) scattering lengths by

$$a_{l\alpha}(+) = A_{l\alpha} + \frac{B_{l\alpha}S_{l\alpha}}{2} \; ; \quad a_{l\alpha}(-) = A_{l\alpha} - \frac{B_{l\alpha}(S_{l\alpha}+1)}{2} . \qquad (2.29)$$

Thus we see that direct scattering is both coherent and incoherent while interference scattering is coherent; moreover, only incoherent scattering is spin-dependent. When more than one isotope is present in the system the scattering amplitudes should be replaced by appropriate isotopic averages.[9]

We will now briefly indicate the essential connection between the present **formalism and Van Hove's** approach.[24] The differential cross section for a monatomic system is*

$$\sigma(\epsilon_i,\Omega,\epsilon_f)=\frac{a^2 k_f}{2\pi N k_i}\int dt\, e^{-i\epsilon t}\sum_{\ell\ell'}\langle e^{itH}\, e^{i\underline{K}\cdot\underline{R}_\ell}\, e^{-itH}\, e^{-i\underline{K}\cdot\underline{R}_{\ell'}}\rangle_T ,$$

where the symbol a is used to denote the appropriate scattering length. If a function $G(r,t)$ is defined as

$$G(\underline{r},t)=(2\pi)^{-3}\int d^3K\, e^{-i\underline{K}\cdot\underline{r}}\sum_{\ell\ell'}\langle e^{itH}\, e^{i\underline{K}\cdot\underline{R}_\ell}\, e^{-itH}\, e^{-i\underline{K}\cdot\underline{R}_{\ell'}}\rangle_T ,$$

then the cross section can be calculated in terms of $G(\underline{r},t)$ by means of a four-dimensional Fourier transform,

$$\sigma(\epsilon_i,\Omega,\epsilon_f)=\frac{a^2 k_f}{2\pi N k_i}\, S(\underline{K},\epsilon),$$

$$S(\underline{K},\epsilon)=\int dt\, d^3r\, G(r,t)\, e^{i(\underline{K}\cdot\underline{r}-\epsilon t)}$$

One advantage of this approach lies in the fact that it is possible

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*Vineyard has discussed the generalization to polyatomic systems.[17]

to assign physical interpretation to the function $G(\mathbf{r},t)$ in the classical limit and obtain different methods of calculation.* For then $G(\mathbf{r},t)d^3r\,dt$ represents the probability that given a molecule at the origin at $t=0$ there will be a molecule in d^3r about $\mathbf{r}$ and dt about t. The presentation of experimental data in terms of $S(\mathbf{k},\epsilon)$ have also been proposed.[25,26]

The general expression for the differential cross section (2.27) provides a basis for a direct calculation of the quantity measured in a scattering experiment. The thermal average $\langle \chi_{\ell\ell'} \rangle_{\alpha\alpha',T}$ contains effects of neutron interaction with all possible degrees of freedom of the molecular system, and in order to study characteristic atomic motions in liquids it will be necessary to obtain an appropriate decomposition of (2.27). It is anticipated that because of the relatively small energies $(E \sim 10^{-3} - 10^{-2}\ \mathrm{ev})$ associated with translations of the centers of mass and molecular rotations these motions are apt to be influenced to the greatest extent by existing intermolecular forces in the liquid.** We now make the fundamental assumptions that the energy of the liquid can be represented as a sum of individual molecular energies and that for times long compared to neutron-nuclear interaction times each molecule moves in a potential generated by interactions with its neighbors, which is approximated by a

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*The transition between classical and quantum mechanical $G(\mathbf{r},t)$ functions has been recently discussed by Rosenbaum and Zweifel.[67]

**The internuclear vibrational motions, which involve energies $(E \sim 10^{-1}\ \mathrm{ev})$ large compared to translations and rotations, are less affected by surroundings. It is known that the frequencies of normal vibrations are different in the liquid phase from those in the corresponding vapor; however, even for water where considerable amount of hydrogen bonding exists in the liquid state the changes in the frequencies are no more than 5-10%.[31]

function depending upon the coordinates of that molecule only and is taken to be the sum of two terms. One of these is assumed to be a function only of the center-of-mass coordinates and the other a function of molecular orientation. Thus

$$H_S = \sum_{\ell} H_{\ell} , \tag{2.29}$$

and

$$H_{\ell} = H^{\ell}_{T} + H^{\ell}_{R} + H^{\ell}_{V} . \tag{2.30}$$

According to (2.29) the physical many-body problem is reduced to a single-particle description, and in (2.30) the energy of each polyatomic molecule is further separated into energies of translation, rotation, and vibration. The present treatment will ignore couplings between different degrees of freedom. The dynamical correlation effects among molecules are treated in terms of effective interaction potentials which are single-particle potentials, and evidently, such a description of the liquid state emphasizes aspects characteristic of individual particle motions. Because the model does not take into account explicit correlations in positions and orientations of the molecules it is not expected to be suitable for direct studies of molecular symmetries.

The form of the Hamiltonian (2.30) suggests a decomposition for the position of a nucleus measured in the laboratory system,

$$\underline{r}_{\ell\alpha} = \underline{R}_{\ell} + \underline{b}_{\ell\alpha} + \underline{u}_{\ell\alpha} , \tag{2.31}$$

where $\underline{R}_\ell$ is the position of center of mass of the ℓth molecule, $\underline{b}_{\ell\alpha}$ the equilibrium position of the αth nucleus in the ℓth molecule and $\underline{u}_{\ell\alpha}$ its instantaneous displacement. When the molecule consists of more than two atoms nuclear vibrations can be treated in terms of normal coordinates, which are obtained by a transformation of the form,

$$\underline{u}_{\ell\alpha} = \sum_\lambda \underline{c}^\lambda_{\ell\alpha} q_\lambda \,, \tag{2.32}$$

where $\underline{c}^\lambda$ is the λth polarization vector associated with normal coordinate q_λ. Among the components in (2.31) $\underline{R}_\ell, \underline{b}_{\ell\alpha}, q_\lambda$ will not commute with H^ℓ_T, H^ℓ_R, H^ℓ_V respectively, and in addition $\underline{c}_{\ell\alpha}$, a vector which rotates with the molecule, also does not commute with H^ℓ_R;^{4} otherwise all commutators vanish. The thermal average (2.28) is therefore factored into a product,

$$\langle \chi_{\substack{\ell\ell' \\ \alpha\alpha'}} \rangle_T = \langle e^{itH^\ell_T} e^{i\underline{\kappa}\cdot\underline{R}_\ell} e^{-itH^\ell_T} e^{-i\underline{\kappa}\cdot\underline{R}_{\ell'}} \rangle_T \langle \chi^I_{\substack{\ell\ell' \\ \alpha\alpha'}} \rangle_T \tag{2.33}$$

$$\langle \chi^I_{\substack{\ell\ell' \\ \alpha\alpha'}} \rangle_T = \langle e^{itH^\ell_R} e^{i\underline{\kappa}\cdot\underline{b}_{\ell\alpha}} e^{itH^\ell_V} e^{i\underline{\kappa}\cdot\sum_\lambda \underline{c}^\lambda_{\ell\alpha} q_\lambda} e^{-itH^\ell_R} e^{-itH^\ell_V} e^{-i\underline{\kappa}\cdot\sum_\lambda \underline{c}^\lambda_{\ell'\alpha'} q_\lambda} e^{-i\underline{\kappa}\cdot\underline{b}_{\ell'\alpha'}} \rangle_T \tag{2.34}$$

The nonseparability of rotation and vibration in $\langle \chi^I \rangle_T$ results from the commutation relation noted above and also follows directly from the decomposition (2.31) since only three coordinates are needed to specify each $\underline{r}_{\ell\alpha}$ and the coordinates of $\underline{b}_{\ell\alpha}$ and $\underline{u}_{\ell\alpha}$ are clearly not independent sets.

Because the operators in each thermal average involve only the ℓth and ℓ' molecules, the matrix elements therefore are taken with respect to the appropriate coordinates of these two molecules. It is seen that $\langle \zeta_{\ell\ell'} \rangle_{\alpha\alpha' T}$ will be time-dependent only when $\ell = \ell'$, so energy transfer is possible only by direct and "inner" scatterings. The fact that intermolecular interference is a purely elastic effect arises from the assumption of no explicit dynamical correlations among the molecules.

In the following chapters we shall be concerned with neutron scattering by associated or polar liquids. Specific dynamical models describing molecular translations and rotations will be proposed and the corresponding thermal averages evaluated. It will be assumed that average over molecular orientations in the rotational and vibrational thermal averages can be performed separately, although the coupling effect can be formally treated by the methods developed later.* This assumption corresponds to ignoring the effect of rotation of the axes of vibration during a scattering event.

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*It has been shown in the calculation of angular distribution of neutrons scattered by CH_4 vapor that little error is introduced by ignoring the nonseparability of rotational and vibrational thermal averages.[2]

CHAPTER III

MOLECULAR TRANSLATIONS

The translational motion of a molecule is influenced only by its interactions with the surroundings. In a gas the molecules tend to behave as free particles whereas in a crystal they would tend to oscillate about their respective lattice sites. Unfortunately, for molecules in the liquid state no simple description of their translational degrees of freedom is available primarily because these molecules neither diffuse continuously nor remain in any oscillatory state over a long period of time. It is however reasonable for some class of experiments to suppose that the molecules would vibrate in a semistable structure for a certain length of time after which diffusion takes place by activation through potential barriers created by intermolecular interactions, and the entire process then repeats itself.

In recent neutron experiments with water[12-14] and liquid tin[10] solid-like behavior has been observed which suggests the existence of a certain degree of local order in the liquid. For the description of neutron scattering by polar molecules we feel it is appropriate, particularly in view of the appreciable molecular associations, to adopt a quasi-crystalline model in which it is assumed that the neutron will encounter, on the average, a molecule oscillating about a position of temporary equilibrium rather than one undergoing diffusive motions. Similar description has been used by Morales[15] in analyzing neutron diffraction by liquid lead, and by Singwi and Sjölander[18] in calculating the differential cross section for water. In both cases the results are in better agreement with measurements than those obtained assuming continuous diffusion.

The present chapter is devoted to a discussion of attempts to justify the assumption of hindered molecular translations. We shall derive an approximate effective potential in terms of the Stockmayer two-particle interaction where, under a certain condition to be satisfied by the associated parameters, the potential may be approximated by a three-dimensional isotropic harmonic oscillator potential. Such an approximation would effectively correspond to an Einstein-crystal description of the liquid in which liquid parameters are used to determine the force constant.

The oscillator model thus obtained is then used to calculate the direct and interference scattering contributions to the differential cross section from center-of-mass motions. Similar calculations for a square-well potential, an alternative to the parabolic approximation, have also been considered and are discussed in Appendix C.

THE EFFECTIVE POTENTIAL

We consider a molecule in a pure liquid moving in the field of its neighbors. The energy of interaction for this molecule, which, according to independent-particle assumption, is the same for any molecule in the system, can be written as

$$V = \int U(\underline{R},\underline{\mu};\underline{R}',\underline{\mu}')\,f(\underline{R}|\underline{R}',\hat{\underline{\mu}},\hat{\underline{\mu}}')\,d^3R'\,d\Omega(\hat{\underline{\mu}})\,d\Omega(\hat{\underline{\mu}}'), \qquad (3.1)$$

where $U(\underline{R},\underline{\mu};\underline{R}',\underline{\mu}')$ is the two-particle interaction for a molecule at $\underline{R}$ with dipole moment $\underline{\mu}$ and another at $\underline{R}'$ and dipole moment $\underline{\mu}'$, and $f\,d^3R'\,d\Omega(\hat{\underline{\mu}})\,d\Omega(\hat{\underline{\mu}}')$ is the probability that given a molecule at $\underline{R}$ its dipole orientation is in $d\Omega(\hat{\underline{\mu}})$ about $\hat{\underline{\mu}}$ *and* that another molecule is in d^3R' about $\underline{R}'$ with dipole orientation in $d\Omega(\hat{\underline{\mu}}')$ about $\hat{\underline{\mu}}'$. The integrations in (3.1) extend over all configuration space excluding the volume occupied by the molecule in question and over all orientations of both dipoles. The frequency f may be decomposed into a product of two frequencies,

$$f(\underline{R}|\underline{R}',\hat{\underline{\mu}},\hat{\underline{\mu}}')\,d^3R'\,d\Omega(\hat{\underline{\mu}})\,d\Omega(\hat{\underline{\mu}}') = \qquad (3.2)$$

$$F(\underline{R}|\underline{R}')\,d^3R'\;P(\underline{R},\underline{R}'|\hat{\underline{\mu}},\hat{\underline{\mu}}')\,d\Omega(\hat{\underline{\mu}})\,d\Omega(\hat{\underline{\mu}}'),$$

where $F(\underline{R}|\underline{R}')\,d^3R'$ is the probability that given a molecule at $\underline{R}$ there will be another in d^3R' about $\underline{R}'$, and $P(\underline{R},\underline{R}'|\hat{\underline{\mu}},\hat{\underline{\mu}}')\,d\Omega(\hat{\underline{\mu}})\,d\Omega(\hat{\underline{\mu}}')$ is the probability that given a molecule at $\underline{R}$ and another at $\underline{R}'$ the former will have dipole orientation in $d\Omega(\hat{\underline{\mu}})$ about $\hat{\underline{\mu}}$ and the latter will have dipole orientation in $d\Omega(\hat{\underline{\mu}}')$ about $\underline{\mu}'$.

A useful approximation for treating $F(\underline{R}|\underline{R}')$, first used by Lennard-Jones and Devonshire[32] in attempts to calculate thermodynamic properties of dense gases and more recently applied by Morales[15] to neutron scattering by normal liquids, is to assume that all the neighboring molecules which interact with the molecule under consideration to an appreciable extent are uniformly distributed on the surface of a sphere centered about the "equilibrium" position of the molecule and whose radius is of the order of intermolecular separation.* In applying such a "smearing" procedure we first write

$$\begin{aligned} F(\underline{R}|\underline{R}')\,d^3\underline{R}' &= F(|\underline{R}-\underline{R}'|)\,d^3\underline{R}' \\ &\simeq F(|\underline{x}-\underline{R}'|)\,d^3\underline{R}' \qquad (3.3) \\ &\simeq F(\underline{\xi})\,d^3\underline{\xi} \ , \end{aligned}$$

where the various position vectors are defined in Fig. 2. Now according to the Lennard-Jones and Devonshire approximation,

$$F(\underline{\xi}) = \frac{\zeta}{4\pi s^2}\,\delta(\underline{\xi}-s) \ , \qquad (3.4)$$

where ζ is the number of neighboring molecules involved in the interaction and s is the mean separation between molecules. It is expected that ζ should be of the order of coordination number for the corresponding crystal and s may be estimated from the radial distribution function studied in X-ray scattering.

In choosing a two-particle interaction $U(\underline{R},\underline{\mu};\underline{R}',\underline{\mu}')$ it is evident that any reasonable potential should be attractive at large molecular separations and repulsive when the molecules are close together. In ad-

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*The assumption of the existence of "equilibrium" positions is central to the quasi-crystalline model which we have adopted. At least for neutron scattering this is believed to be reasonable since neutron-nuclear interaction times are very short compared to times required for molecules to change their positions appreciably.

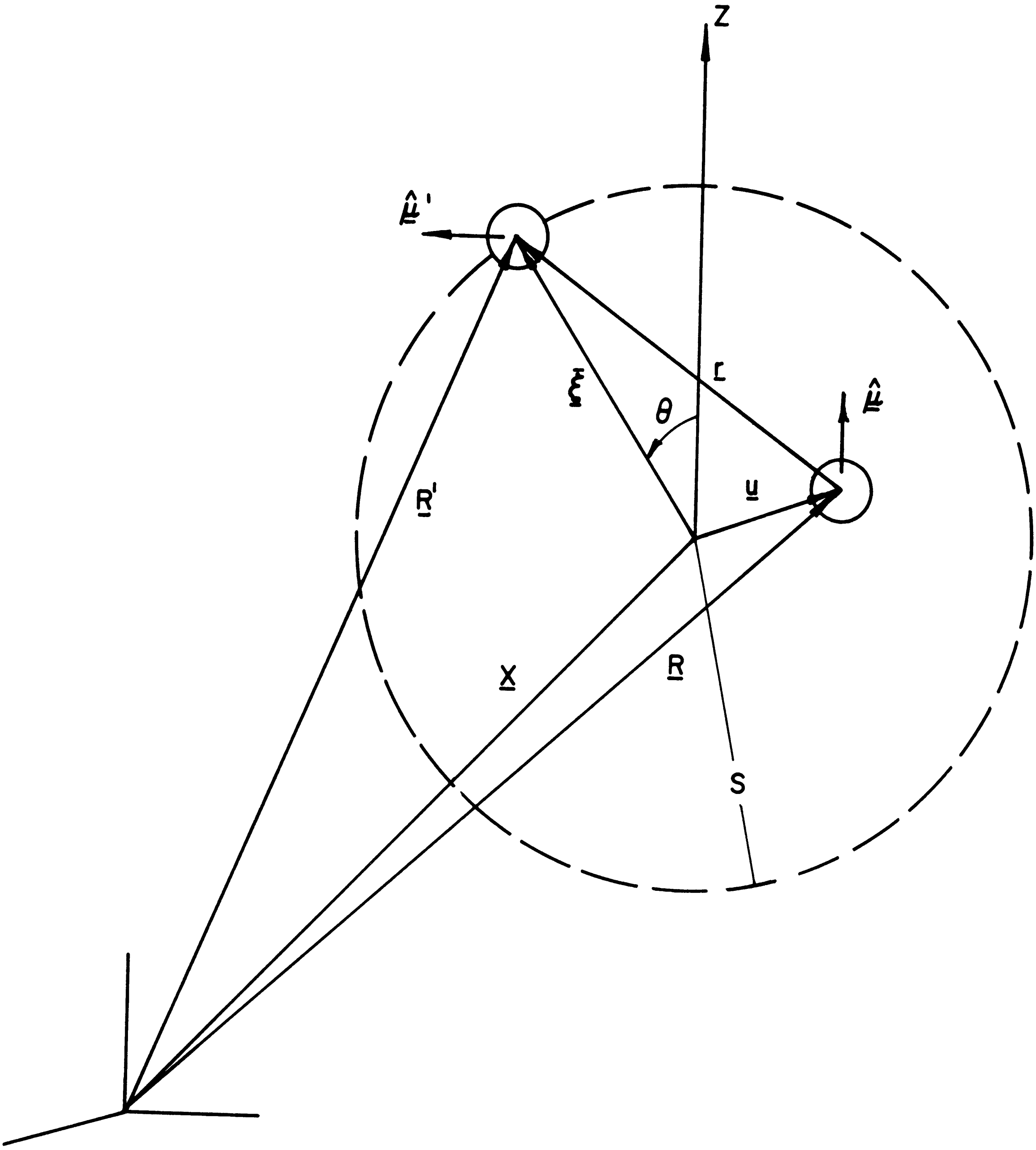

Fig. 2. Position vectors for the Lennard-Jones-Devonshire "smearing" procedure.

dition, the potential should be orientation-dependent to account for electrostatic interactions between dipoles. Such a potential can be constructed by taking a central potential widely known as the Lennard-Jones 6-12 potential and the interaction between two rigid, point dipoles. The resulting potential is the Stockmayer potential,[33]

$$U = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + U_d , \qquad (3.5)$$

$$U_d = \frac{\underline{\mu}\cdot\underline{\mu}'}{r^3} - \frac{3(\underline{\mu}\cdot\underline{r})(\underline{\mu}'\cdot\underline{r})}{r^5} , \qquad (3.6)$$

with $\underline{r} = \underline{R}' - \underline{R}$. In (3.5) constants ϵ and σ are characteristic of the chemical species of the molecule; ϵ is the maximum energy of attraction of the two molecules which occurs at a separation of $2^{1/6}\sigma$, and σ is the distance of closest approach.

Now it remains to obtain an explicit expression for $P(\underline{R},\underline{R}'|\hat{\underline{\mu}},\hat{\underline{\mu}}')$. From the form of the two-particle potential just chosen it follows that at a given intermolecular separation there will be relative orientations for which U_d is a minimum or maximum. The fact that statistically molecules prefer those orientations for which the interaction energy is small can be expressed by means of the Boltzmann factor $e^{-\beta U_d}$, where $\beta = (kT)^{-1}$, k being the Boltzmann constant and T the absolute temperature of the liquid. The effective potential (3.1) now becomes

$$V = \int d^3\xi\, F(\xi)\left\{4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \overline{U}_d\right\} , \qquad (3.7)$$

where

$$\bar{U}_d = \left[\int e^{-\beta U_d}\, d\Omega(\hat{\underline{\mu}})\, d\Omega(\hat{\underline{\mu}}')\right]^{-1} (\times) \int U_d\, e^{-\beta U_d}\, d\Omega(\hat{\underline{\mu}})\, d\Omega(\hat{\underline{\mu}}') . \tag{3.8}$$

It has been assumed in (3.8) that any variation in $\underline{r}$ during a period of rotation can be neglected. At small separations or low temperatures $\bar{U}_d \sim (U_d)_{min}$ because the molecules will tend to oscillate only about the orientation corresponding to minimum energy. For large separations and high temperatures the Boltzmann factor can be expanded in powers of $(kT)^{-1}$. The first nonvanishing contribution to $\bar{U}_d$ is[33]

$$\bar{U}_d \simeq -\frac{2\mu^2}{3kTr^6} \tag{3.9}$$

The dipole-dipole interaction averaged in the above manner is seen to be attractive and vanishes as $(kT)^{-1}$ for large temperatures. Using (3.4) and (3.9) we obtain

$$V = 2z\epsilon_0 \int_{-1}^{1} \left[\left(\frac{\sigma_0}{|\underline{s}-\underline{u}|}\right)^{12} - \left(\frac{\sigma_0}{|\underline{s}-\underline{u}|}\right)^{6}\right] d(\cos\theta), \tag{3.10}$$

where ϵ_0, σ_0 are constants chosen so the integrand has the same form as the Lennard-Jones 6-12 potential,

$$\epsilon_0 = \epsilon(1+t)^2 \quad , \quad \sigma_0 = \sigma(1+t)^{-1/6} \tag{3.11}$$

with $t = 3\mu^4(8\epsilon\sigma^6 kT)^{-1}$. After a trivial integration,

$$V(u) = \frac{\alpha}{y}\left\{\gamma\left[(1-y)^{-10} - (1+y)^{-10}\right] + (1+y)^{-4} - (1-y)^{-4}\right\}, \tag{3.12}$$

where $\alpha = \frac{3\epsilon_0}{2}\left(\frac{\sigma_0}{s}\right)^6$, $\gamma = \frac{2}{5}\left(\frac{\sigma_0}{s}\right)^6$, and $y = \frac{u}{s}$. Thus V(u) is only a function of the displacement of the molecule from its "equilibrium" position, and the shape of this isotropic potential is characterized entirely by the parameter γ . At the origin u = 0, V(u) has the value $-8\left(\frac{\sigma_0}{s}\right)^6$.

It is necessary to introduce further approximations of V(u). This is because the Schrödinger equation with (3.12) as the potential energy cannot be solved analytically and numerical solutions for the wave functions are not suitable for later calculations of the differential cross section. In Fig. 3 we show a number of typical curves for V(u) with different values of γ . As we would expect, the associative nature of the dipole-dipole interaction tends to cause the molecule to move away from its "equilibrium" position. However, beyond a certain point the repulsive part of the potential becomes dominant quickly and the molecule is thus always bound. Moreover, for $\gamma \gtrsim 5\times10^{-2}$ the potential can be reasonably approximated by either a square well or a parabola. In either case the approximation results in one parameter for the present model, the width of the well or the strength of the restoring force. By considering the expansion of V(u) in a power series about u = 0, we find that in order for the potential to have a minimum only at the origin in the range $y<1$, the condition

$$4.4\left(\frac{\sigma_0}{s}\right)^6 > 1 \qquad (3.13)$$

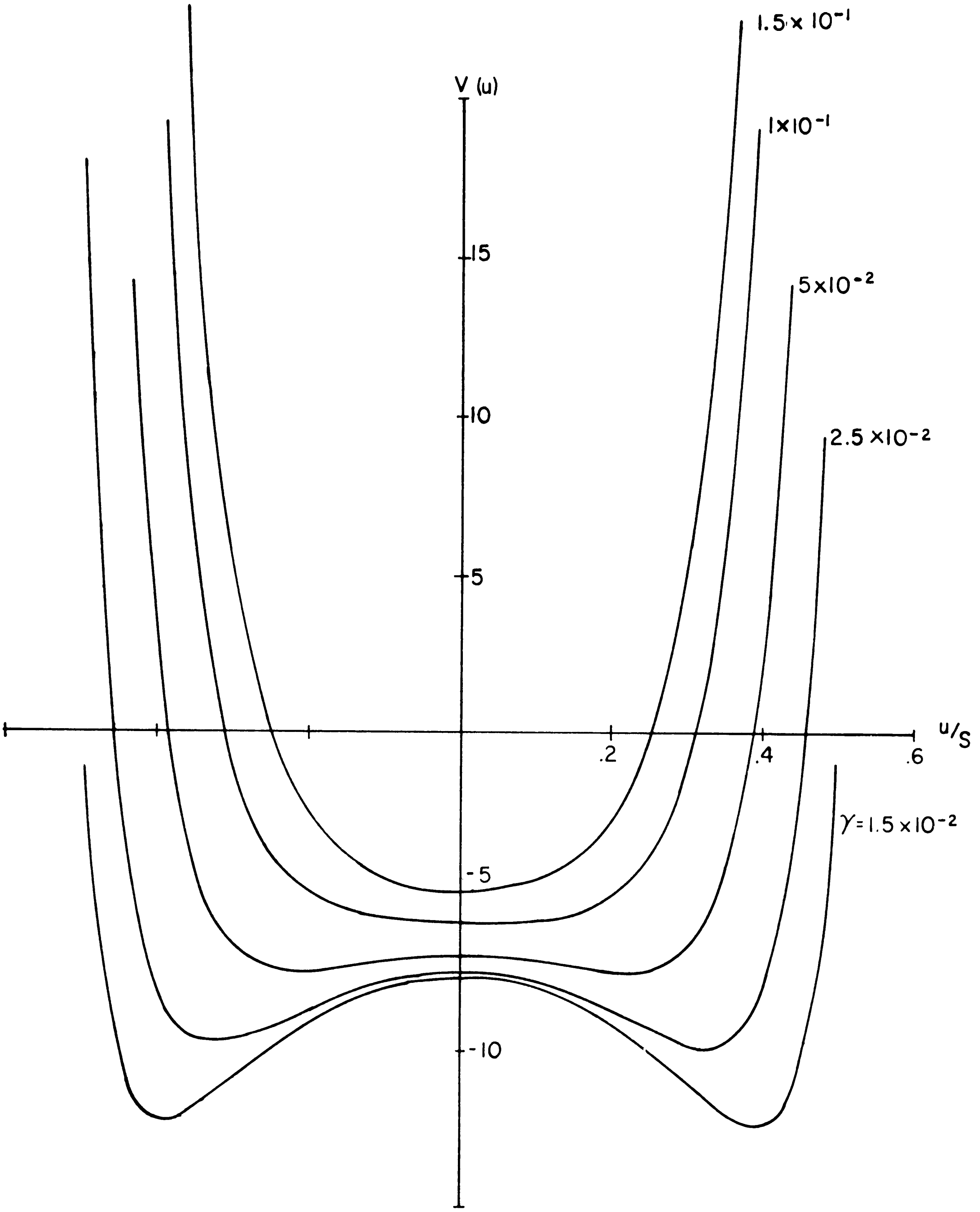

Fig. 3. Curves of the effective potential V(u) in units of χ .

must be satisfied.* For liquids whose parameters are such that (3.13) holds,** a first estimate of the oscillator frequency in the parabolic approximation is given by $\left[\frac{1}{M}\left(\frac{d^2V}{du^2}\right)_{u=0}\right]^{1/2}$. We suspect that even when the above condition is not met the use of an oscillator potential is at least consistent with the fundamental assumption of quasi-crystalline behavior of polar molecules in the liquid state. The present description ignores diffusive motion which certainly must exist: for this reason usefulness of the model is questionable in considerations of long-term phenomena such as those encountered in thermodynamic measurements.

For special cases where it is felt that dipole-dipole interactions should result in a significant anisotropic character of the effective potential, a slightly different method may be used. We may assume a fixed relative orientation between the molecules and relegate any directional effects to an asymmetrical distribution of the neighbors. For simplicity the dipole orientation of the neighbors can be taken to be the same as that of the central molecule, a choice that is actually quite reasonable except when $\underline{\mu}\cdot\underline{r} = 0$, in which case the molecular dipoles will tend to point in opposite directions. This particular approximation leads to an expression for the effective potential,

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*This condition with $\mu = 0$ has been noted by Morales[15] in connection with deriving an effective potential for normal liquids.

**Using the parameters given by Hirschfelder, Curtiss, and Bird,[33] p. 214, we have found that the oscillator approximation is justified, on the basis of condition (3.13), in the cases of $CHCl_2F$ (dichlorofluoromethane, $\gamma \cong 0.403$), C_2H_5Cl (ethyl chloride, $\gamma \cong 0.654$), and possibly CH_3Cl (methyl chloride, $\gamma \cong 0.0795$).

$$V = \int U(\underline{r},\underline{\mu})P(\underline{\xi})d^3\underline{\xi} \qquad (3.14)$$

where

$$U(\underline{r},\underline{\mu}) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \frac{\mu^2}{r^3} - \frac{3(\underline{\mu}\cdot\underline{r})^2}{r^5} ,$$

and $P(\underline{\xi})$ specifies the nonspherical distribution. Calculations have been made assuming the neighbors are "smeared" over the surface of a spheroid and are discussed in Appendix A.

THE THERMAL AVERAGE

The preceding discussions indicate that a tractable description of molecular translations in polar liquids is obtained by treating the molecules as a system of independent oscillators. Using such a model we shall proceed to calculate the thermal average appropriate to the translational degrees of freedom. The analysis involved can be considerably simplified by introducing time-dependent operator formalism,[1] in fact, it will be seen that explicit form of the molecular wave function is never needed in obtaining the necessary matrix elements.

The thermal average is first written as

$$\left\langle e^{itH_T^{\ell}} e^{i\underline{K}\cdot\underline{R}_{\ell}} e^{-itH_T^{\ell}} e^{-i\underline{K}\cdot\underline{R}_{\ell'}} \right\rangle_T = e^{i\underline{K}\cdot(\underline{X}_{\ell}-\underline{X}_{\ell'})} \left\langle e^{i\underline{K}\cdot\underline{R}_{\ell}(t)} e^{-i\underline{K}\cdot\underline{R}_{\ell'}} \right\rangle_T \qquad (3.15)$$

where

$$\underline{R}_{\ell}(t) = e^{itH_T^{\ell}} \underline{R}_{\ell} e^{-itH_T^{\ell}} = \underline{X}_{\ell} + \underline{u}_{\ell}(t) \qquad (3.16)$$

is the Heisenberg operator. The "equilibrium" position vector $\underline{x}$ is not a dynamical variable and therefore appears only in the multiplicative phase factor. Both time-dependent and time-independent forms of the instantaneous displacement vector are used, the time-independent operator $\underline{u}$ being the same as u(t) at t = 0. The case of $\ell = \ell'$ corresponds to direct and "inner" scattering while that of $\ell \neq \ell'$ corresponds to interference scattering. In the former case, it is evident that corresponding components of $\underline{U}_\ell(t)$ and $\underline{U}_\ell$ will not commute, and in the latter case all components commute with each other regardless of time-dependence. We shall consider direct scattering first.

Because the Hamiltonian H_T^ℓ is separable into three independent components the thermal average (3.15) for $\ell = \ell'$ factors into a product of three thermal averages, one for each component,

$$\langle e^{i\underline{K}\cdot\underline{R}_\ell(t)}\, e^{-i\underline{K}\cdot\underline{R}_{\ell'}} \rangle_T = \prod_{i=1}^{3} \sum_{n_i} P_{n_i} \langle n_i | e^{iK_iU_i(t)}\, e^{-iK_iU_i} | n_i \rangle, \qquad (3.17)$$

the subscript ℓ being suppressed and n_i is the quantum number specifying the ith component of the molecular translational wave function. In arriving at (3.17) use has been made of the fact that P_n is similarly expressible as a product of P_{n_i}. In thermodynamic equilibrium we have explicitly

$$\begin{aligned} P_{n_i} &= e^{-2n_iz} \Big(\sum_{n_i} e^{-2n_iz} \Big)^{-1} \\ &= e^{-2n_iz} (1 - e^{-2z}), \end{aligned} \qquad (3.18)$$

where $z = \frac{\hbar\omega}{2kT}$, ω being the frequency which characterizes the oscillator potential. Because in the present instance the effective potential describing translations is a three-dimensional isotropic oscillator potential each thermal average in the product can be treated identically. By virtue of the operator identity[9]

$$e^{A}e^{B} = e^{A+B+\frac{1}{2}[A,B]}, \tag{3.19}$$

which holds whenever A and B commute with their commutator [A,B],

$$\langle e^{i\kappa u(t)}e^{-i\kappa u}\rangle_T = e^{\frac{\kappa^2}{2}[u(t),u]}\langle e^{i\kappa[u(t)-u]}\rangle_T, \tag{3.20}$$

where we have suppressed index i, and the commutator [u(t),u] is just a number. Next we make use of Bloch's theorem,[1]

$$\langle e^{Q}\rangle_T = e^{\frac{1}{2}\langle Q^2\rangle_T}, \tag{3.21}$$

Q being a multiple, or some linear combination, of commuting oscillator coordinates and their conjugate momenta. Thus

$$\langle e^{i\kappa u(t)}e^{-i\kappa u}\rangle_T = e^{-\frac{\kappa^2}{2}[\langle u^2(t)\rangle_T+\langle u^2\rangle_T-2\langle u(t)u\rangle_T]}. \tag{3.22}$$

A more detailed discussion of the time-dependent operator u(t) is given in Appendix B. It is shown that u(t) can be expressed in terms of the "creation" and "annihilation" operators a(t) and $a^+(t)$. The thermal averages in (3.22), evaluated in terms of thermal averages of a(t), $a^+(t)$ and their time-independent analogues, are

$$\langle u^2(t)\rangle_T = \langle u^2\rangle_T = \frac{\hbar}{2M\omega}\left\{2\langle n\rangle_T + 1\right\},$$

$$\langle u(t)u\rangle_T = \frac{\hbar}{2M\omega}\left\{(\langle n\rangle_T + 1)\, e^{-i\omega t} + \langle n\rangle_T\, e^{i\omega t}\right\}, \qquad (3.23)$$

where

$$\langle n\rangle_T = \sum_n n P_n = e^{-2z}(1 - e^{-2z})^{-1}. \qquad (3.24)$$

After some rearrangements we arrive at the expression for direct scattering

$$\langle e^{i\underline{K}\cdot\underline{R}_l(t)}\, e^{-i\underline{K}\cdot\underline{R}_l}\rangle_T = e^{-DK^2}\sum_{n=-\infty}^{\infty} I_n(PK^2)\, e^{-n(z-i\omega t)}, \qquad (3.25)$$

where

$$D = \frac{\hbar}{2M\omega}\coth z,$$

$$P = \frac{\hbar}{2M\omega}\operatorname{csch} z,$$

and we have used the generating function of the modified Bessel function of the first kind,[34]

$$e^{\frac{1}{2}y(t+\frac{1}{t})} = \sum_{n=-\infty}^{\infty} t^n I_n(y).$$

In a very similar manner the corresponding result for interference scattering is found to be

$$\langle e^{i\underline{K}\cdot\underline{R}_l(t)}\, e^{-i\underline{K}\cdot\underline{R}_{l'}}\rangle_T = \langle e^{i\underline{K}\cdot\underline{R}_l}\rangle_T \langle e^{-i\underline{K}\cdot\underline{R}_{l'}}\rangle_T$$

$$= e^{-DK^2}\, e^{i\underline{K}\cdot(\underline{x}_l - \underline{x}_{l'})}. \qquad (3.26)$$

The time-dependence of the thermal average determines the manner in which energy may be exchanged with the neutron in a collision. To illustrate this remark more explicitly we imagine the differential cross section (2.20) to depend only upon the translational degrees of freedom of the system. In this case the "time" integration yields delta functions which obviously represent statements of energy conservation. For direct scattering we would obtain terms containing $\delta(\epsilon - n\hbar\omega)$ which, depending on the sign of n, correspond to neutron energy gain or loss in multiplies of the oscillator energy spacing. Of course not all negative values of n are allowed since the neutron cannot give more than its incident energy to the liquid. The energy distribution of the scattered neutrons, according to the oscillator model, therefore exhibits a certain uniform and discrete structure consisting of peaks whose amplitudes decrease with increasing amount of energy transfer. This structure is in marked contrast to the smooth distribution of energies predicted by the gas model. In fact, the comparison of the calculated distribution with measurements provides a direct means with which it is possible to determine whether a gas or an oscillator model offers the more appropriate description of the translational degrees of freedom.

At any finite temperature neutron energy loss is always more probable then energy gain since the lower system states are more heavily populated. This fact is expressed by the factor e^{-nz}. In particular, at T = 0 energy gain is no longer possible. When the molecules are more tightly bound, the frequency ω will be large and in the limit all inelastic term vanish by virtue of the small-argument representation, $I_n(x) \simeq (n!)^{-1}(x/2)^n$. This is to be expected on physical grounds as a system of rigidly-fixed molecules cannot possibly exchange energy with the neutron. Elastic scattering (n = 0), however, is still allowed.

It is seen that the thermal average for interference scattering is time-independent and thus leads to no energy transfer. The reason for interference scattering being a purely elastic effect lies in the assumption of no dynamical correlations among molecules, a situation in which it is highly improbable for neutron waves to be scattered from two uncorrelated scattering centers with identical energy exchanges. The phase factor $e^{i\underline{\kappa}\cdot(\underline{x}_\ell-\underline{x}_{\ell'})}$ is ultimately to be summed over all ℓ and ℓ' molecules $(\ell \neq \ell')$. To do so explicitly would require the determination of these "equilibrium" positions relative to each other. This difficulty can be avoided if we follow the earlier method of smearing the neighbors over the surface of a sphere, then

$$N^{-1}\sum_{\ell\ell'}{}' e^{i\underline{\kappa}\cdot(\underline{x}_\ell-\underline{x}_{\ell'})} \simeq \frac{\sin \kappa s}{\kappa s} , \tag{3.27}$$

where s is the mean intermolecular separation. Alternatively, we may adopt a more elaborate treatment of the summation in terms of the radial distribution function[15] or simply apply Debye's outer-effect approximation well known in X-ray diffraction.[35]

The exponential $e^{-D\kappa^2}$ which appears in both (3.25) and (3.26) is the Debye-Waller factor originally derived in X-ray scattering to account for temperature effects. This factor attenuates the intensity of all scattering processes particularly at high temperature or small ξ. In addition to being temperature-dependent it also varies with the angle of scattering. For sufficiently small ξ, PK^2 will be large so $I_n(x) \simeq (2\pi x)^{-1/2} e^{x}$, and the Debye-Waller factor is thus canceled. This implies that at high temperatures or large momentum transfer only direct scattering will be appreciable.

We have just used a quasi-crystalline model to study neutron scattering by the translational degrees of freedom of molecules in the liquid state. The general expressions derived here will be used to calculate energy distributions of neutrons scattered by water and hydrogen chloride, and the results will be compared to corresponding distributions based on the gas model.[1] In the case where observable differences can be shown to exist in distributions according to the two models a scattering experiment will then be suggested. Because the present thermal average calculation is actually applicable to any bound system in which interparticle interactions may be approximated by harmonic forces, similar cross section results can also be used to study neutron scattering by vibrational degrees of freedom of molecules. In fact, the treatment applies equally well to analysis of neutron diffraction by crystals,* the significant difference being the appearance of the well-known Bragg condition for interference which would not be obtained for liquids.

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*Neutron diffraction by crystals have been discussed by a number of authors. For an excellent review readers may see Kothari and Singwi;[8] a number of fundamental aspects have also been examined in detail by Yip, Osborn, and Kikuchi.[9]

CHAPTER IV

MOLECULAR ROTATIONS

When the energy of incident neutrons is very low ($\epsilon_i \sim 10^{-3} - 10^{-2}$ ev) the scattered neutron energy distribution can be significantly affected by angular momentum exchanges resulting from neutron interaction with the rotational degrees of freedom of the scattering molecule. The problem of inelastic scattering by rigid molecules rotating freely in space has been treated in terms of the Sachs-Teller mass tensor[2] which combines the effects of molecular translations with rotations, and also from the point of view of computing inelastic corrections[1,36] to the static approximation which ignores energy transfer. In this section a formal calculation is described in which matrix elements in the thermal average are evaluated rigorously. The present approach has been used independently by Rahman[37]* following the work of Gorgunov.[38] Because of the assumption of free rotational motions the results are applicable primarily to gases and normal liquids; the effects of intermolecular forces will be considered in the following chapter in terms of a specific model for polar molecules.

We shall begin with a review of the dynamics of molecular rotations in free space. The purpose for the review is to present a complete development of those aspects of the molecular problem relevant to the

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*We wish to thank Dr. K.S. Singwi for bringing this work to our attention.

analysis of neutron scattering. In addition, certain features of the free-rotator problem which are also pertinent to later development of a description of hindered molecular rotation can be brought forth.

DYNAMICS OF FREE MOLECULAR ROTATIONS*

Consider an arbitrary polyatomic molecule rotating freely in space as a rigid body with energy

$$H_R = \frac{1}{2}\left(\frac{P_x^2}{I_x} + \frac{P_y^2}{I_y} + \frac{P_z^2}{I_z} \right), \tag{4.1}$$

where P_i and I_i are the ith components of the total angular momentum and moment of inertia respectively in the "body" system, i.e., that system of axes fixed in the molecule which coincide with the principal axes. It is conventional to express this energy as

$$\frac{2}{c} H_R = a P^2 + P_z^2 + b(P_x^2 - P_y^2), \tag{4.2}$$

with

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

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

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

If I_y is assigned the intermediate value of the three moments, then $-1 \leq b \leq 0$. In (4.2) we also have the Hamiltonians for symmetric mol-

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*A large amount of literature is available; for review reader may see Nielsen[39] and Van Winter.[40]

ecules ($I_x = I_y$) and spherical molecules ($I_x = I_y = I_z$). The Eulerian angles ($\psi\theta\varphi$) which specify the orientation of the body axes relative to a set of axes fixed in space are defined in Fig. 4. In terms of these dynamical variables explicit expressions of the angular momentum operators have been derived and are given in Appendix D.

It is convenient to treat the symmetric molecule first and then use the result to obtain solutions for other cases. The eigenvalue problem is

$$(H_{SR} - E)\Phi(\psi\theta\varphi) = 0 , \tag{4.3}$$

where from (4.2)

$$H_{SR} = \frac{P^2}{2I} + \frac{(I - I_z)}{2II_z} P_z^2 , \tag{4.4}$$

with $I_x = I_y = I$, and from Appendix D,

$$H_{SR} = -B\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right) + \frac{(I-I_z)}{I_z}\frac{\partial^2}{\partial\varphi^2}\right] , \tag{4.5}$$

with $B = \hbar^2/2I$. In (4.5) the coefficient of every term is independent of ψ and φ, the equation is therefore separable. The solution becomes

$$\Phi(\psi\theta\varphi) = e^{iM\psi} e^{iK\varphi} R(\theta) , \tag{4.6}$$

where M, K are integers, and $R(\theta)$ is defined by the equation

$$R'' + \cot\theta R' - \left[\frac{(M - K\cos\theta)^2}{\sin^2\theta} - \lambda\right] R = 0 , \tag{4.7}$$

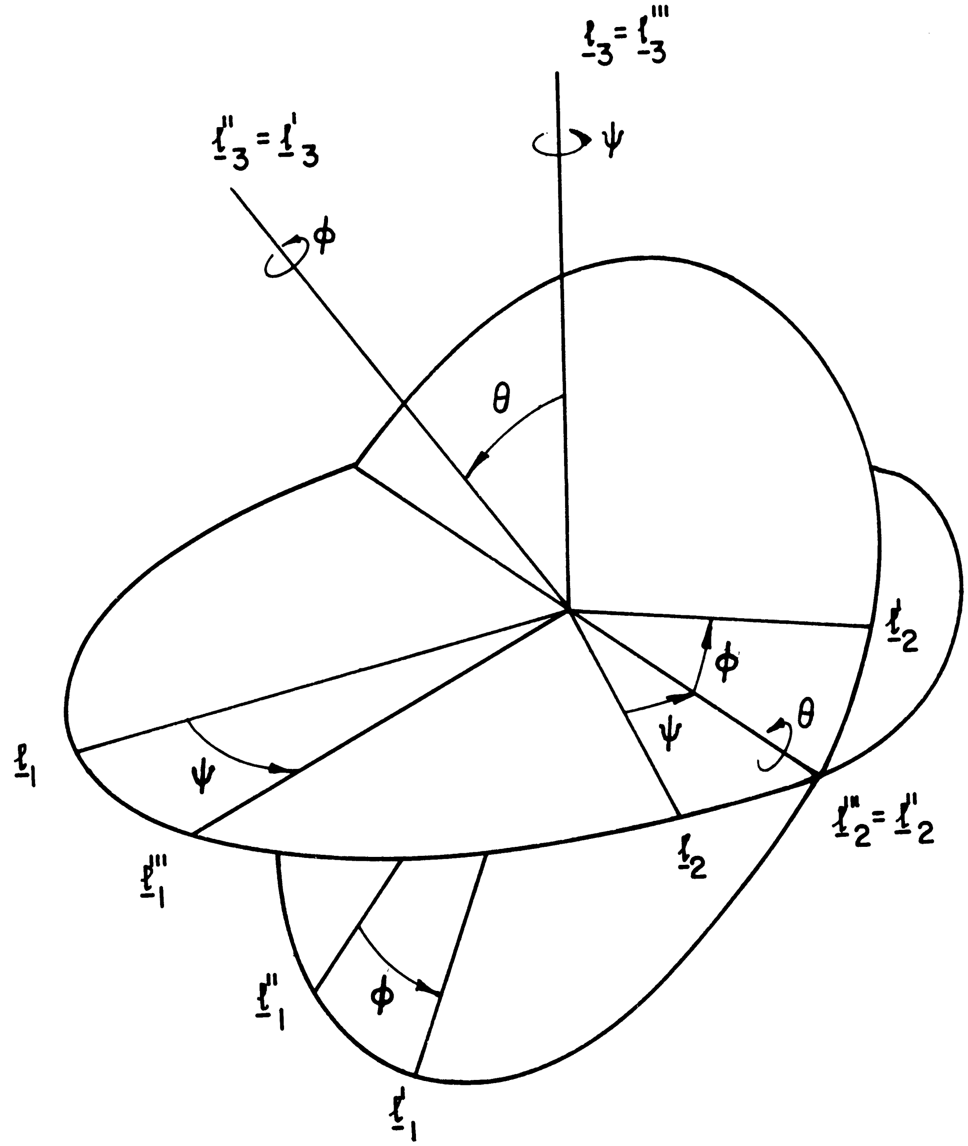

Fig. 4. Eulerian angles ($\psi\theta\phi$) defining orientation of body axes $\underline{\ell}_i'$ with respect to space axes $\underline{\ell}_i$.

with $\lambda = \frac{E}{B} - \frac{I}{I_z} K^2$. This equation can be solved by studying its singular points. A variable transformation $2t = 1 - \cos\theta$ leads to

$$t(1-t)R''(t) + (1-2t)R' - \left[\frac{(M-K+2Kt)^2}{4t(1-t)} - \lambda\right]R = 0, \qquad (4.8)$$

with regular singular points at t = 0, 1 and another regular singular point at infinity which is nonphysical since t is defined in the range (0, 1). In the neighborhood of the first two singular points the well-behaved solutions are

$$\begin{aligned} R(t) &\underset{t\to 0}{\sim} t^{|K-M|/2} , \\ &\underset{t\to 1}{\sim} (1-t)^{|K+M|/2} \end{aligned} \qquad (4.9)$$

The transformation is therefore suggested,

$$R(t) = t^{|K-M|/2} (1-t)^{|K+M|/2} F(t) . \qquad (4.10)$$

After some manipulations, an equation for F(t) is obtained,

$$t(1-t)F'' + [\gamma - (\alpha+\beta+1)t]F' - \alpha\beta F = 0, \qquad (4.11)$$

with

$$\begin{aligned} \gamma &= |K-M| + 1 \\ \alpha+\beta &= |K-M| + |K+M| + 1 \\ \alpha\beta &= (|K+M| + |K-M|)(|K+M| + |K-M| + 2)/4 - K^2 - \lambda . \end{aligned} \qquad (4.12)$$

Equation (4.11) is known as the hypergeometric equation which is the standard equation for three regular singular points.[41] The analytic solution at t = 0 is called the hypergeometric function, expressible as a convergent series for $|t| < 1$,

$$F(t) = 1 + \frac{\alpha\beta}{\gamma} t + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)2!} t^2 + \cdots \quad . \tag{4.13}$$

Since the wave function must be finite everywhere (including t = 1) the series must terminate. This will be the case if α is a negative integer or zero. Thus it follows that the energy eigenvalues are given by

$$E_{JKM} = BJ(J+1) + \frac{B(I-I_z)}{I_z} K^2 , \tag{4.14}$$

where $-\alpha+\frac{1}{2}(|K+M|+|K-M|)$ is denoted by J, J = 0, 1,...; K,M = 0, ±1,..., ±J. The corresponding eigenfunction is

$$|JKM\rangle = \Phi_{JKM}(\psi\theta\varphi) = N e^{iM\psi} e^{iK\varphi} t^{|K-M|/2} (1-t)^{|K+M|/2} F(\alpha,\beta;\gamma|t), \tag{4.15}$$

and[39]

$$N^2 = \frac{(|K+M|+|K-M|+1-2\alpha)!(|K+M|+|K-M|-\alpha)!(|K-M|-\alpha)!}{4\pi^2(-\alpha)!(|K-M|)!^2(|K+M|-\alpha)!} . \tag{4.16}$$

In the solutions just obtained J, K, M are quantum numbers appropriate to the total angular momentum, its component along the body-z axis and its component along the space-z axis. Since P^2 commutes with P_z in both systems then the total angular momentum and its two z components are all conserved. From this standpoint the energy E_{JKM} could have been written down directly. The fact that the energy is independent of M is not surprising because the molecule has no preferred orientations in space. Associated with this randomness is a degeneracy of 2J+1. The energy is also independent of the sign of K, corresponding to clockwise or counter clockwise rotations about its symmetry axis, hence each state $|JKM\rangle$ is 2(2J+1)-fold degenerate.

A convenient representation of the symmetric-molecule wave function has been given by Wigner[42]

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^J_{-M,-K}(\psi\theta\varphi) \;, \tag{4.17}$$

where if we follow the notation used by Rose[43]

$$D^J_{MK}(\psi\theta\varphi) = e^{-iM\psi}\, d^J_{MK}(\theta)\, e^{-iK\varphi} \;, \tag{4.18}$$

$$d^J_{MK}(\theta) = \left[(J+K)!\,(J-K)!\,(J+M)!\,(J-M)!\right]^{1/2}$$

$$(x) \sum_s (-)^s \frac{\left(\cos\frac{\theta}{2}\right)^{2J+K-M-2S} \left(-\sin\frac{\theta}{2}\right)^{M-K+2S}}{(J-M-S)!\,(J+K-S)!\,(S+M-K)!\,S!} \;. \tag{4.19}$$

Summation over s is such that arguments in all the factorials are never negative. The function D^J_{MK} is known as the rotation matrix, or the MKth matrix element of the Jth irreducible unitary representation of the rotation group. Because of its well-known symmetry and transformation properties[43] this function is very useful in the calculation of maxtrix elements.

Solutions for the spherical molecule are obtained by simply setting $I_z = I$ in the above results. The complete degeneracy in K leads to a total degeneracy of $(2J+1)^2$. The wave functions and energies of a linear molecule can also be derived as a special case in which there is no rotation about the molecular axis. Thus

$$|JM\rangle = Y_J^M(\theta,\psi) = \left[\frac{(2J+1)(J-|M|)!}{4\pi(J+|M|)!}\right]^{1/2} e^{iM\psi} P_J^M(\cos\theta) \qquad (4.20)$$

$$= \left(\frac{2J+1}{4\pi}\right)^{1/2} D^{J*}_{M0}(\psi\theta 0), \qquad (4.21)$$

$$E_{JM} = BJ(J+1), \qquad (4.22)$$

where P_J^M is an associated Legendre polynomial. Degeneracy for this system with only two degrees of freedom is 2J+1.

We next consider the general case of the asymmetrical molecule whose energy is given by (4.2) or

$$\frac{2}{c}H_{AR} = \frac{2}{c}H_{SR} + bH_1 . \qquad (4.23)$$

The eigenvalue problem

$$\left[\frac{2}{c}H_{AR} - \nu\right]\Psi(\psi\theta\phi) = 0, \qquad (4.24)$$

with $\nu = \frac{2}{c}E$, may be treated by noting that the states $|JKM\rangle$ form a complete set in the space of the Eulerian angles and thus provide a basis for the expansion of the present solution

$$|JEM\rangle = \sum_{K=-J}^{J} \alpha_K |JKM\rangle . \qquad (4.25)$$

The coefficients α depend only upon K because J and M are still good quantum numbers (P^2 and the space-z component still commute with H_{AR}).

Now quantum number E is anticipated here as a replacement for K. Equation (4.24) becomes

$$\sum_{K'} \alpha_{K'} \left[\left(\tfrac{2}{c} E_{JK} - \nu \right) \delta_{KK'} + b \langle JK | H_1 | JK' \rangle \right] = 0 , \qquad (4.26)$$

where we have suppressed the label M. As usual there will be no nontrivial solution for α_K unless the secular determinant vanishes, i.e.,

$$\det \left| \left(\tfrac{2}{c} E_{JK} - \nu \right) \delta_{KK'} - b \langle JK | H_1 | JK' \rangle \right| = 0 . \qquad (4.27)$$

Since K ranges from -J to J the determinant yields 2J+1 values of ν , each of which will be labeled by the index E. The energy of an asymmetric molecule is therefore given by $c\nu_{JE}/2$, where for a given J, E may range from zero to 2J in integral steps. For a given J and E, the appropriate set of coefficients of expansion are then obtained from the set of simultaneous equations (4.26).

The present method of solution corresponds to an orthogonal transformation from an "old" basis $\{ |JKM\rangle \}$ to a "new" basis $\{ |JEM\rangle \}$ in which H_{AR} is diagonal. In order to evaluate the matrix element $\langle JK | H_1 | JK' \rangle$ the "raising" and "lowering" angular momentum operators $P_{\pm} = P_x \pm iP_y$ can be introduced. Thus

$$H_1 = P_x^2 - P_y^2 = \tfrac{1}{2} (P_+^2 + P_-^2) . \qquad (4.28)$$

In terms of $P_{\pm}$ the necessary computation is greatly simplified because the symmetric-molecule wave function, denoted here as $|JK\rangle$, transforms according to the Jth irreducible representation of the rotation group, and under the operation of infinitesimal rotation operators $P_\pm$ yields[48]

$$P_\pm |JK\rangle = \hbar\sqrt{(J\mp K)(J\pm K+1)}\,|JK\pm 1\rangle\,. \qquad (4.29)$$

In other words,

$$H_1 |JK\rangle = \frac{\hbar^2}{2}\left\{ g(J,K+1)|JK+2\rangle + g(J,K-1)|JK-2\rangle \right\}, \qquad (4.30)$$

with

$$g(J,K) = \sqrt{(J-K)(J-K+1)(J+K)(J+K+1)}\,. \qquad (4.31)$$

Thus H_1 couples only adjacent states $K' = K\pm 2$.*

The determinant (4.27) has the tridiagonal form

$$\begin{vmatrix}
\hbar^2J^2-\Omega_{JE} & 0 & b\langle JJ|H_1|JJ-2\rangle & & & \\
0 & \ddots & \ddots & \ddots & & \\
b\langle JJ-2|H_1|JJ\rangle & \ddots & \ddots & \ddots & \ddots & \\
 & \ddots & \hbar^2 1-\Omega_{JE} & 0 & b\langle J1|H_1|J-1\rangle & \\
 & & 0 & \ddots & \ddots & \ddots \\
 & & b\langle J-1|H_1|J1\rangle & \ddots & \ddots & \ddots \\
 & & & \ddots & \ddots & \hbar^2J^2-\Omega_{JE}
\end{vmatrix} = 0, \qquad (4.32)$$

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*The same result is obtained by using the differential-operator form of H_{AR} and deriving recursion relations for the wave functions (4.15).[44]

where $\Omega_{JE} = \nu_{JE} - a\hbar^2 J(J+1)$. The energy of the molecule is therefore

$$E_{JEM} = \frac{c}{2}\left[a\hbar^2 J(J+1) + \Omega_{JE}\right], \tag{4.33}$$

and the associated eigenfunctions are given by (4.25). The (2J+1)-fold degenerary due to the arbitrary orientation of the space-z axis still remains; however, previous degeneracy in the sign of K is removed by the asymmetry.

THE THERMAL AVERAGE

The wave functions and energies of rigid molecules obtained in the preceding section can now be used to investigate neutron scattering by a system with only rotational degrees of freedom. From the standpoint of energy transfer the case of interest is the scattering from a single molecule since "outer" scattering is necessarily elastic in the present model. The appropriate thermal average will be evaluated first for symmetric molecules, then the asymmetrical case can be derived as a generalization.*

For molecules with axial symmetry the matrix elements under consideration are

$$\langle \alpha\alpha'; JKM\rangle = \langle JKM|\, e^{itH_{SR}}\, e^{i\underline{\kappa}\cdot\underline{b}_\alpha}\, e^{-itH_{SR}}\, e^{-i\underline{\kappa}\cdot\underline{b}_{\alpha'}}\, |JKM\rangle \tag{4.34}$$

$$= \sum_{J'K'M'} e^{it(E_{JK}-E_{J'K'})} \langle JKM|\, e^{i\underline{\kappa}\cdot\underline{b}_\alpha}\, |J'K'M'\rangle\langle J'K'M'|\, e^{-i\underline{\kappa}\cdot\underline{b}_{\alpha'}}\, |JKM\rangle ,$$

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*Rahman[37] has independently obtained results similar to those derived here.

the index ℓ being suppressed since $\ell = \ell'$. In the product only one matrix element needs to be obtained, the other is merely its complex conjugate with appropriate change of nuclear subscript. The equilibrium position $\underline{b}$ is a constant vector in the body system while neutron momentum transfer $\underline{K}$ is fixed in space; in the scalar product both vectors must be expressed in the same system of coordinates. A useful expansion for the purpose of calculating the indicated matrix elements is

$$e^{i\underline{K}\cdot\underline{b}} = 4\pi \sum_{\ell k} i^{\ell} j_{\ell}(Kb) Y_{\ell}^{k*}(\hat{\underline{b}}') Y_{\ell}^{k}(\hat{\underline{K}}') \, , \tag{4.35}$$

where 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 body axes. Because $\underline{K}$ is specified in the laboratory, a rotation yields

$$Y_{\ell}^{k}(\hat{\underline{K}}') = \sum_{m} D_{-m,-k}^{\ell}(\psi\theta\varphi) Y_{\ell}^{m}(\hat{\underline{K}}) \, , \tag{4.36}$$

where $\hat{\underline{K}}$ has components in the space system. The rotation matrix D_{mk}^{ℓ} is an explicit function of the Eulerian angles describing rotations of the molecule with respect to the space axes. The desired matrix element now becomes $\langle JKM | D_{-m,-k}^{\ell} | J'K'M' \rangle$.

The expectation value of D_{mk}^{ℓ} in an eigenstate of the symmetric molecule is easily obtained since the wave functions are themselves rotation matrices. The product of rotation matrices can be reduced by means of the tabulated Clebsch-Gordon coefficients $C_{m_1\ m_2\ m_1+m_2}^{j_1\ j_2\ j_3}$; the relevant reduction formula as well as other useful properties of the

Clebsch-Gordon coefficients are summarized below:*

$$D^{\ell}_{mk} D^{J}_{MK} = \sum_{\lambda=|J-\ell|}^{J+\ell} C^{\ell\, J\, \lambda}_{m\, M}\, C^{\ell\, J\, \lambda}_{k\, K}\, D^{\lambda}_{m+M\;\, k+K}$$

$$\begin{aligned} C^{j_1\, j_2\, j_3}_{m_1\, m_2} &= (-)^{j_1+j_2-j_3} C^{j_1\, j_2\, j_3}_{-m_1\, -m_2} \\ & \quad (-)^{j_1+j_2-j_3} C^{j_2\, j_1\, j_3}_{m_2\, m_1} \\ & \quad (-)^{j_1-m_1} \left(\frac{2j_3+1}{2j_2+1}\right)^{1/2} C^{j_1\, j_3\, j_2}_{m_1\, -m_3} \\ & \quad (-)^{j_2+m_2} \left(\frac{2j_3+1}{2j_1+1}\right)^{1/2} C^{j_3\, j_2\, j_1}_{-m_3\, m_2} \\ & \quad (-)^{j_1-j_3+m_2} \left(\frac{2j_3+1}{2j_1+1}\right)^{1/2} C^{j_2\, j_3\, j_1}_{m_2\, -m_3} \end{aligned} \qquad (4.37)$$

$$D^{J*}_{MK} = (-)^{M-K} D^{J}_{-M,-K}$$

$$\sum_{M} C^{J\, J'\, \ell}_{M\;\, m-M}\, C^{J\, J'\, \ell'}_{M\;\, m-M} = \delta_{\ell\ell'}$$

$$\sum_{J} C^{\ell\, J'\, J}_{k\;\, K-k}\, C^{\ell\, J'\, J}_{k'\;\, K-k'} = \delta_{kk'}$$

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*See Rose[43] for a thorough discussion of the properties of rotation matrix and Clebsch-Gordon coefficients.

Using these results we obtain

$$\langle JKM| e^{i\underline{K}\cdot\underline{b}} |J'K'M'\rangle = (-)^{M'+K}\sqrt{(2J+1)(2J'+1)}$$

$$(\times)\sum_{\ell} i^{\ell}\left(\frac{4\pi}{2\ell+1}\right)^{1/2} j_{\ell}(Kb)\, Y_{\ell}^{K'-K}(\hat{\underline{b}})\, C^{J\ J'\ \ell}_{M\ -M'\ 0}\, C^{J\ J'\ \ell}_{-K\ K'}\ , \tag{4.38}$$

where use has been made of the orthogonality property

$$\int d\Omega(\psi\theta\varphi)\, D^{J*}_{MK} D^{\ell}_{mk} = \frac{8\pi^2}{2J+1}\,\delta_{J\ell}\,\delta_{Mm}\,\delta_{Kk}\ . \tag{4.39}$$

In arriving at (4.38) the space-z axis is chosen to be along $\hat{\underline{K}}$ so that $Y_{\ell}^{m}(\hat{\underline{K}}) = \delta_{m0}\sqrt{(2\ell+1)/4\pi}$.

The energy eigenvalues of the symmetric molecule have been shown to be degenerate with respect to M and the sign of K. The matrix element (4.34) therefore should be averaged over K, -K and the 2J+1 values of M. Summation over M and M' gives

$$\sum_{MM'} C^{J\ J'\ \ell}_{M\ -M'\ 0}\, C^{J\ J'\ \ell'}_{M\ -M'\ 0} = \delta_{\ell\ell'}\ , \tag{4.40}$$

and we have

$$\begin{aligned}\langle\alpha\alpha';JK\rangle &= \frac{1}{2(2J+1)}\sum_{\pm K,M}\langle\alpha\alpha';JKM\rangle \\ &= \frac{1}{2}\sum_{J'|K'|}(2J'+1)\, e^{it(E_{JK}-E_{J'K'})}\end{aligned} \tag{4.41}$$

$$(\times)\sum_{\substack{\pm K\ \pm K'\\ \ell}}\left(\frac{4\pi}{2\ell+1}\right) j_{\ell}(Kb_{\alpha})\, j_{\ell}(Kb_{\alpha'})\, Y_{\ell}^{K'-K}(\hat{\underline{b}}_{\alpha})\left[Y_{\ell}^{K'-K}(\hat{\underline{b}}_{\alpha'})\right]^{*}\left[C^{J\ J'\ \ell}_{K\ -K'}\right]^{2}.$$

The thermal average for scattering by a single symmetric molecule thus becomes

$$\langle \alpha\alpha' \rangle_T = \langle e^{itH_{SR}} e^{i\underline{K}\cdot\underline{b}_\alpha} e^{-itH_{SR}} e^{-i\underline{K}\cdot\underline{b}_{\alpha'}} \rangle_T$$

$$= \Big(\sum_{J|K|} e^{-\beta E_{JK}}\Big)^{-1} \sum_{J|K|} \langle \alpha\alpha' ; JK \rangle \, e^{-\beta E_{JK}} \qquad (4.42)$$

Inelastic neutron interaction with rotational degree of freedom results in angular momentum exchanges which are governed by selection rules for J' and K' for fixed values of J and K. The energy transfer depends upon ℓ, which from the expansion (4.35) is interpretable as the amount of angular momentum exchanged in the collision. When $\ell = 0$, we would expect only elastic scattering; this is precisely the case since K' = K and the Clebsch-Gordon coefficients require J' = J. Explicitly,

$$C^{J\;J'\;\ell}_{K\;-K'} \xrightarrow[\ell=0]{} (2J+1)^{-1} \delta_{JJ'} \qquad (4.43)$$

and so

$$\langle \alpha\alpha' ; JK \rangle_{\ell=0} = j_0(Kb_\alpha)\, j_0(Kb_{\alpha'}) \,. \qquad (4.44)$$

As b → 0 only the term with $\ell = 0$ survives in (4.41) because $j_\ell(x) \xrightarrow[x=0]{} j_0(x)\delta_{\ell 0}$; the vanishing of the "moment arm" therefore renders the scattering process purely elastic. Equation (4.44) is, however, not the sole elastic contribution to the cross section since for finite angular momentum exchanges there will also be selection rules for K' = K and

$J' = J$, and each term in the ℓ-sum contributes to elastic scattering. The Clebsch-Gordon coefficient $C^{J\,J'\,\ell}_{K\,-K'}$ restricts J' to range from $|J-\ell|$ to $J+\ell$, then for small Kb the spherical Bessel function $j_\ell(x) \simeq x^\ell/(2\ell+1)!!$ limits inelastic processes to small energy transfer.

Spherical and linear molecules are special cases of some interest in which rotational energy is the same and depends only upon quantum number J. The difference in these two cases lies in system symmetries and hence the associated degeneracies as noted previously. The matrix elements in the thermal average must be appropriately averaged over all orientations with respect to which the energy is degenerate. The results are

$$\langle\alpha\alpha'\rangle_T = \Big(\sum_J e^{-\beta E_J}\Big)^{-1} \sum_J \langle\alpha\alpha';J\rangle\, e^{-\beta E_J}, \tag{4.45}$$

where for spherical molecules,

$$\begin{aligned}\langle\alpha\alpha';J\rangle &= (2J+1)^{-2}\sum_{KM}\langle\alpha\alpha';JKM\rangle \\ &= (2J+1)^{-1}\sum_{J'}(2J'+1)\,e^{it(E_J-E_{J'})}\sum_{\ell k}\frac{4\pi}{2\ell+1}\, j_\ell(Kb_\alpha)\, j_\ell(Kb_{\alpha'})\, Y^{k}_\ell(\hat{b}'_\alpha)\, Y^{k*}_\ell(\hat{b}'_{\alpha'}) \sum_K \Big[C^{J'\,J\,\ell}_{K+k\,-K}\Big]^2 \\ &= (2J+1)^{-1}\sum_{J'}(2J+1)\,e^{it(E_J-E_{J'})}\sum_{\ell=|J-J'|}^{J+J'} j_\ell(Kb_\alpha)\, j_\ell(Kb_{\alpha'})\, P_\ell(\theta_{\alpha\alpha'}),\end{aligned} \tag{4.46}$$

where $\theta_{\alpha\alpha'}$ is the angle between $\hat{\underline{b}}_\alpha$ and $\hat{\underline{b}}_{\alpha'}$. Similarly for linear molecules,

$$\begin{aligned}\langle\alpha\alpha';J\rangle &= (2J+1)^{-1}\sum_M\langle\alpha\alpha';JM\rangle \\ &= \sum_{J'} e^{it(E_J-E_{J'})}\sum_\ell (2\ell+1)(2\delta_{\alpha\alpha'}-1)^\ell\, j_\ell(Kb_\alpha)\, j_\ell(Kb_{\alpha'})\Big[C^{J\,\ell\,J'}_{0\,0}\Big]^2.\end{aligned} \tag{4.47}$$

The absence of the degree of freedom characterized by K results in $(2J'+1)/(2J+1)$ being replaced by $(2\ell+1)\left[C^{J\,\ell\,J'}_{0\,0\,0}\right]^2$.

The present method of obtaining the thermal average can be generalized to the case of an asymmetric molecule in a straightforward manner. We recall from the discussion of the molecular problem that the wave function of the asymmetric molecule is expressible as a linear combination of $|JKM\rangle$, and that the energy is still degenerate with respect to M. The eigenstates are

$$|JEM\rangle = \sum_{\alpha=-K}^{K} \alpha_{JEK} |JKM\rangle , \qquad (4.48)$$

where the coefficients α_{JEK} are real and the energy eigenvalues are labeled by J and E. Following the same procedure as before, we obtain the formal expression

$$\langle \alpha\alpha' \rangle_T = \Big(\sum_{JE} e^{-\beta E_{JE}} \Big)^{-1} \sum_{JE} \langle \alpha\alpha' ; JE \rangle e^{-\beta E_{JE}}$$

$$\begin{aligned} \langle \alpha\alpha' ; JE \rangle &= (2J+1)^{-1} \sum_{M} \langle \alpha\alpha' ; JEM \rangle \\ &= \sum_{J'E'} (2J'+1) e^{it(E_{JE}-E_{J'E'})} \sum_{KK'\ell kk'} \frac{4\pi}{2\ell+1} j_\ell(\kappa b_\alpha) j_\ell(\kappa b_{\alpha'}) \qquad (4.49) \\ &(x)\; Y_\ell^{k}(\hat{\underline{b}}_\alpha) Y_\ell^{k'*}(\hat{\underline{b}}_{\alpha'}) \alpha_{JEK} \alpha_{J'E'K+k} \alpha_{JEK'} \alpha_{J'E'K'+k'} C^{J\;J'\;\ell}_{K\;-(K+k)} C^{J\;J'\;\ell}_{K'\;-(K'+k')} \end{aligned}$$

In the results derived thus far the scattering process is treated by explicit summation of individual rotational transitions. While the approach is rigorous and accounts for all the inelastic processes at once, the amount of labor involved in an actual calculation may be prohibitively large if the incident neutron energy is sufficiently high as to induce a great number of transitions. On the other hand the results obtained here are in a form suitable for exhibiting the low energy limit. By virtue of the small argument representation for the spherical Bessel function, $j_\ell(x) \simeq \frac{x^\ell}{(2\ell+1)!!}\left[1 - \frac{x^2}{2(2\ell+3)} + \cdots\right]$, the cross section may be readily expressed as series in powers of $K_\nu b$.

When the incident energy is large compared to rotational level spacings the mass-ratio expansion method developed by Zemach and Glauber[1] and extended by Volkin[36] can be applied. The static approximation, or the high-energy approximation which completely ignores inelastic scattering, may be readily deduced from the present expressions for spherical and linear molecules.[37] In this case energy transfer is a small fraction of the incident energy so K_ν is essentially only a function of k_i and the angle of scattering; moreover, the time-dependent factor will be ignored and the sum over J' extended to all possible final states. Then from (4.46)

$$(2J+1)^{-1}\sum_{J'K}(2J'+1)\left[C^{J'\,J\,\ell}_{K+k\,-K}\right]^2 = \frac{2\ell+1}{2J+1}\sum_{K}\sum_{J'}\left[C^{\ell\,J\,J'}_{-k\,-K}\right]^2 = 2\ell+1 , \qquad (4.50)$$

and

$$\begin{aligned}\langle\alpha\alpha'\rangle_T &\simeq \sum_\ell (2\ell+1)\, j_\ell(K_\nu b_\alpha)\, j_\ell(K_\nu b_{\alpha'})\, P_\ell(\theta_{\alpha\alpha'}) \\ &= j_0(K_\nu|\mathbf{b}_\alpha - \mathbf{b}_{\alpha'}|) .\end{aligned} \qquad (4.51)$$

The last step in (4.51) can be shown by considering expressions similar to (4.35) for $e^{i\underline{K}\cdot(\underline{b}-\underline{b}')}$ and $e^{i\underline{K}\cdot\underline{b}}\, e^{-i\underline{K}\cdot\underline{b}'}$, and then integrate over all directions of $\hat{\underline{K}}$. The same result can be derived for linear molecules using (4.47), thus implying that the scattering of high-energy neutrons is not sensitive to system symmetries. In the cases of spherical and linear molecules the scattering is also not influenced by the particular state in which the molecule is found initially.

CHAPTER V

HINDERED MOLECULAR ROTATIONS

The preceding analysis of neutron scattering by systems with only rotational degrees of freedom assumes the molecules are freely rotating. The assumption would be erroneous if existing intermolecular electrostatic effects in the liquid are sufficiently strong as to cause the molecules to spend considerable period of time in certain preferred orientations of minimum energy. This type of motion is then said to be hindered in the sense that one or more of the rotational degrees of freedom is partially or completely restrained.

Recent slow-neutron experiments with water[12,13] have revealed pronounced inelastic scattering involving energies larger than any characteristic energies associated with molecular translations or free rotations and smaller than the vibrational energies. As in early interpretations of similar observations in Raman spectra,[22] the specific atomic motions responsible for this type of energy transfer are taken to be hindered rotations, or torsional oscillations of the molecule in the potential field of its neighbors.[12]

In this section we propose a dynamical model for the description of hindered as well as free rotational motions. The basis of the model lies in the assumption that the hindrances are predominantly produced by electrostatic interactions among molecular dipoles and because of the appreciable amount of crystalline symmetry still persisting in the liquid strong direction-dependent forces prevent the molecules from having complete freedom in rotation. It is evident that this viewpoint is consistent with the model developed earlier for molecular translations.

The present approach treats the interactions of a molecular dipole with its neighbors in terms of the coupling between the dipole moment and a local electric field which represents the effects of the surrounding. As in the previous determination of an effective potential for translations, only one parameter appears in the model to account for the dynamical characteristics of different liquids. The electric field in this connection will be taken as uniform in the immediate neighborhood of the molecule and constant in time, at least during a period of rotation; its magnitude is presumably of the same order as the crystalline field in the corresponding solid phase.*

In the single-particle description the potential for rotations appropriate to our model is just $-\underline{\mu}\cdot\underline{E}$, the interaction of a dipole $\underline{\mu}$ in a uniform electric field $\underline{E}$. The Hamiltonian now becomes

$$H_R' = H_R - \underline{\mu}\cdot\underline{E} , \qquad (5.1)$$

where H_R is the free-rotator Hamiltonian used in the preceding chapter. The direction $\underline{E}$ is fixed for the molecular problem; however, in evaluating the corresponding thermal average its direction must be averaged,

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*Spatial and time dependences of such a field can be assigned physical meanings and may be introduced as modifications of the model.

in which case $\underline{E}$ will be assumed to have random orientation.

In the presence of the potential the total angular momentum is not conserved although with proper choice of coordinates its two z components will still commute with H_R'. We shall first consider a rigorous solution of the molecular problem for symmetric molecules and then indicate a possible generalization to the asymmetric case in Appendix E. It will be seen that the rigorous approach is not convenient for the calculation of thermal average because the determination of rotator energy and wave function requires substantial amount of numerical work. Moreover, as the existence of hindered rotations implies large local electric fields, strong-field solutions should be physically meaningful and capable of providing a suitable means for the analysis of slow-neutron scattering.

A FORMAL SOLUTION

The eigenvalue problem for a symmetric polar molecule rotating in a uniform electric field is*

$$(H_{SR} - \lambda D^1_{00})|\xi KM\rangle = E_{\xi KM}|\xi KM\rangle , \qquad (5.2)$$

where H_{SR} is given by (4.4), $\lambda = \mu E$, and $D^1_{00} = \cos\theta$ [see Eq. (4.21)]. The dipole moment μ has been chosen along the body-z or $\underline{e}_3'$ axis and electric field $\underline{E}$ along the space-z or $\underline{e}_3$ axis so the potential is simply $-\lambda\cos\theta$. Since the other two Eulerian angles are not affected by $\underline{E}$, M and K re-

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*The same equation is encountered in the study of Stark effects in polar molecules. An application of the present approach to linear molecules has been described by Kusch and Hughes.[45]

main as good quantum numbers while ς is anticipated as a replacement for J. Again making use of the fact that the free-rotator eigenstates form a complete set, we seek an expression for $|\varsigma KM\rangle$ of the form

$$|\varsigma KM\rangle = \sum_J C_J(\varsigma)|JKM\rangle \,. \tag{5.3}$$

The coefficients of expansion are determined from the coupled set of equations

$$\sum_{J'} C_{J'}(\varsigma)\left[(E_J - E_\varsigma)\,\delta_{JJ'} - \lambda\, U_{JJ'}\right] = 0 \,, \tag{5.4}$$

where E_J is the free-rotator energy, indices M and K being temporarily suppressed, and E_ς has yet to be found. The interaction matrix element $U_{JJ'}$ is readily obtained by means of the reduction formula (4.37) and orthogonality integral (4.39),

$$U_{JJ'} \equiv \langle J|D^1_{00}|J'\rangle = G_0(J)\,\delta_{JJ'} + G_+(J)\,\delta_{J'J+1} + G_-(J)\,\delta_{J'J-1} \,, \tag{5.5}$$

with

$$G_0(J) = C^{1\;J\;J}_{0\;-M}\; C^{1\;J\;J}_{0\;-K} \,,$$

$$G_\pm(J) = C^{1\;J\pm1\;J}_{0\;-M}\; C^{1\;J\pm1\;J}_{0\;-K} \,. \tag{5.6}$$

The next step is usually to demand that the determinant formed by the coefficients of $C_{J'}(\varsigma)$ in (5.4) vanish, a condition giving rise to allowed values of E_ς, each of which is then used to obtain a corresponding set of $C_J(\varsigma)$. From (5.5) the matrix $U_{JJ'}$ is seen to be an infinite tridiagonal matrix since J is unrestricted, and for this reason it is not possible to exhibit the solutions in closed form. Nevertheless, by using a method first discussed by Feenberg[46] in connection with perturbation theory the solutions can be given in continued-fraction form which will be suitable for weak-field approximations or numerical computation.

We shall write the energy as*

$$E_S(J) = E_J - \lambda U_{JJ} + \lambda^2 \sum_{p \neq J} \frac{U_{Jp} U_{pJ}}{E_S(J) - \mathcal{E}_{Jp}} \; . \qquad (5.7)$$

An argument is given to E_S for identification purposes since in the event the electric field vanishes the energy given by (5.7) must coincide with the corresponding free-rotator energy. The effect of the potential can therefore be studied at any field strength. The close resemblence of (5.7) to ordinary perturbation theory should not imply that the expression is approximate. Due to the fact that D^1_{00} couples only adjacent levels in addition to having nonzero diagonal matrix elements all terms in λ^3 and higher do not appear. To show this we only need to consider the term in λ^3, which would be ordinarily present,

$$\sum_{\substack{p \neq J \\ q \neq J, p}} \frac{U_{Jp} U_{pq} U_{qJ}}{\left[E_S(J) - \mathcal{E}_{Jp}\right]\left[E_S(J) - \mathcal{E}_{Jpq}\right]} \; .$$

For a fixed J, U_{Jp} requires $p = J \pm 1$ and U_{pq} requires $q = J \pm 2$. Since $U_{JJ'} = 0$ for $J' \neq J, J \pm 1$ then U_{qJ} must vanish.

In view of (5.5) the energy is rigorously given by

$$E_S(J) = E_J - \lambda G_0(J) + \lambda^2 \left\{ \frac{G_+^2(J)}{E_S(J) - \mathcal{E}_{JJ+1}} + \frac{G_-^2(J)}{E_S(J) - \mathcal{E}_{JJ-1}} \right\} , \qquad (5.8)$$

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*See Morse and Feshbach,[41] Chapter 9.

$$\mathcal{E}_{JJ'} = E_{J'} - \lambda G_0(J') + \lambda^2 \sum_{J''\neq J,J'} \frac{U_{J'J''}U_{J''J'}}{E_\varsigma(J) - \mathcal{E}_{JJ'J''}} \,, \tag{5.9}$$

$$\mathcal{E}_{JJ'J''} = E_{J''} - \lambda G_0(J'') + \lambda^2 \sum_{J'''\neq J,J',J''} \frac{U_{J''J'''}U_{J'''J''}}{E_\varsigma(J) - \mathcal{E}_{JJ'J''J'''}} \,, \text{ etc.,}$$

with J' = J±1, J'' = J±2, etc. It is more convenient to cast $E_\varsigma(J)$ into the form of a continued fraction,[41]

$$E_\varsigma(J) = E_J - \lambda G_0(J) +$$

$$\lambda^2 \left\{ \frac{G_+(J)}{E_\varsigma(J) - E_{J+1} + \lambda G_0(J+1) - \dfrac{\lambda^2 G_+(J+1)}{E_\varsigma(J) - E_{J+2} + \lambda G_0(J+2) - \cdots}} \right. \tag{5.10}$$

$$\left. \frac{G_-(J)}{E_\varsigma(J) - E_{J-1} + \lambda G_0(J-1) - \dfrac{\lambda^2 G_-(J-1)}{E_\varsigma(J) - E_{J-2} + \lambda G_0(J-2) - \cdots}} \right\} .$$

The coefficients of expansion corresponding to this energy are similarly obtained,

$$C_J(\varsigma) = 1 \,,$$

$$C_{J\pm1}(\varsigma) = \frac{-\lambda G_\pm^{1/2}(J)}{E_\varsigma(J) - E_{J\pm1} + \lambda G_0(J\pm1) - \dfrac{\lambda^2 G_\pm(J\pm1)}{E_\varsigma(J) - E_{J\pm2} + \cdots}} \,. \tag{5.11}$$

Thus the expansion (5.3) consists of three terms, and it is obvious from these results that as $\lambda \to 0$, $|\varsigma KM\rangle \to |JKM\rangle$ and $E_\varsigma(J) \to E_J$. The present formulation is particularly useful in studying the splitting of the energy levels as the electric field varies.* Since the wave function is expressed

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*The total number of splittings is more easily determined from the strong-field solution. For some numerical results in the case of linear molecules, see Kusch and Hughes.[45]

as a linear combination of the rotation matrices the method used previously can be applied in computing the matrix elements for the thermal average. There is little advantage in this approach, however, as it would be very difficult to treat the physically interesting case of strong electric field to exhibit the nature of hindered rotations. In the following we shall therefore directly seek analytic solutions in the high-field limit.

THE HINDERED ROTATOR

The eigenvalue problem for symmetric polar molecules in an electric field expressed in the form of a differential equation is obtained from (5.1) and (4.5). By choosing $\underline{\mu}$ along $\underline{e}_3'$ and $\underline{E}$ along $\underline{e}_3$ the equation is still separable in the three Eulerian angles, so the wave function is of the form

$$\Lambda(\psi\theta\varphi) = e^{iM\psi} e^{iK\varphi} Y(\theta), \qquad (5.12)$$

and $Y(\theta)$ satisfies

$$\left\{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{(M-K\cos\theta)^2}{\sin^2\theta} - \frac{IK^2}{I_z} + \frac{1}{B}(\lambda\cos\theta + E)\right\}Y(\theta) = 0. \qquad (5.13)$$

It is expected that under the influence of strong field the molecular dipole will tend to be aligned in the direction of $\underline{E}$, thus angle θ is restricted to having small values. A meaningful first approximation is then obtained by a power expansion in θ. To second order,

$$\left\{\frac{d^2}{d\theta^2} + \left(\frac{1}{\theta} - \frac{\theta}{3}\right)\frac{d}{d\theta} - \frac{(K-M)^2}{\theta^2} - \left(\frac{I}{I_z} - \frac{2}{3}\right)K^2 - \frac{M}{3}(K+M) + \frac{\lambda+E}{B} - \frac{\lambda\theta^2}{B}\right\}Y(\theta) = 0. \qquad (5.14)$$

The $\frac{\theta d}{3 d\theta}$ term can be eliminated by a change of variable $Y(\theta) = P(\theta)\, e^{\theta^2/12}$.
A further transformation $x = \eta\theta^2$ yields

$$\left\{ \frac{d}{dx}\left(x \frac{d}{dx}\right) - \frac{1}{4}\left(\frac{\alpha^2}{x} + x - \frac{\beta}{\eta}\right)\right\} P(x) = 0 \,, \tag{5.15}$$

where

$$\begin{aligned} \alpha &= |K-M|^2 \\ \beta &= \frac{\lambda+E}{B} - \left(\frac{I}{I_z} - \frac{2}{3}\right)K^2 - \frac{M}{3}(K+M) \\ \eta^2 &= \frac{\lambda}{2B} - \frac{1}{36} \,, \end{aligned} \tag{5.16}$$

an equation with singularieties at $x = 0, \infty$. In the neighborhood of these points the well-behaved solutions are

$$\begin{aligned} P(x) &\underset{x\to 0}{\sim} x^{|\alpha|/2} \\ &\underset{x\to\infty}{\sim} e^{-x/2} \,. \end{aligned}$$

In the small-angle approximation the range of θ is now $(0,\infty)$ instead of $(0,\pi)$. The asymptotic behavior of P suggests the dependent-variable transformation $P(x) = x^{\frac{|\alpha|}{2}} e^{-\frac{x}{2}} L(x)$ which leads to an equation for L(x),

$$xL'' + (|\alpha|+1-x)L' + \left(\frac{\beta}{4\eta} - \frac{|\alpha|+1}{2}\right)L = 0 \,. \tag{5.17}$$

Equation (5.17) is in the form of confluent hypergeometric equation with regular singular point at x = 0 and an irregular point at x = ∞.[41] The solution, like that of the hypergeometric equation, can be expressed as a convergent series for $|x| < 1$. If we require the wave function to be square integrable over the range $(0,\infty)$ it is necessary that $\varsigma = \frac{\beta}{4\eta} - \frac{|\alpha|+1}{2}$ be a positive integer or zero, in which case the solution is the associated Laguerre polynomial $L_{\varsigma}^{|\alpha|}(x)$. The energy and wave function according to this mode of quantization are

$$|\varsigma KM\rangle = N_{\varsigma KM}\, e^{iM\psi}\, e^{iK\varphi}\, x^{\frac{|K-M|}{2}}\, e^{-\frac{x}{2}}\, L_{\varsigma}^{|K-M|}(x) , \qquad (5.18)$$

$$E_{\varsigma KM} = \sqrt{2\lambda B}\,(2\varsigma + |K-M| + 1) + BK^{2}\left(\frac{I}{I_z} - \frac{2}{3}\right) + \frac{BM}{3}(K+M) - \lambda . \qquad (5.19)$$

In writing these results we have used, to a very good approximation, $\eta^{2} \simeq \frac{\lambda}{2B}$ and $e^{-\theta^{2}/12} \simeq 1$. The normalization constant is determined from a special case of a more general integral discussed in Appendix F,

$$N^{2}_{\varsigma KM} = \frac{\eta\, \varsigma!}{2\pi^{2}\left[(\varsigma + |K-M|)!\right]^{3}} . \qquad (5.20)$$

The wave function and energy of a linear molecule are derivable from (5.18) and (5.19) by simply removing the φ degree of freedom and seting K = 0.

$$|\varsigma M\rangle = N_{\varsigma M}\, e^{iM\psi}\, x^{\frac{|M|}{2}}\, e^{-\frac{x}{2}}\, L_{\varsigma}^{|M|}(x) , \qquad (5.21)$$

$$E_{\varsigma M} = \sqrt{2\lambda B}\,(2\varsigma + |M| + 1) + \frac{BM^{2}}{3} - \lambda . \qquad (5.22)$$

Normalization constant here is that given by (5.20) with K = 0 and less a factor of $(2\pi)^{-1/2}$.

The rotational energies of the symmetric molecule are seen to consist of contributions from both hindered and free motions, the latter being the terms proportional to B. This consequence could have been predicted from the form of the potential which contains only the θ variable. Although each of the three degrees of freedom is involved in hindered rotation, the energy of this type of motion actually depends upon only two numbers. This implies that if the energies of free rotation were ignored then the small-angle approximation leads to a description of the symmetric molecule as a system with effectively two degrees of freedom, and in this sense there is no difference in the dynamical behavior between the symmetric and linear molecules. Moreover, through the form of the energy of hindered motion the nature of the small-angle approximation is revealed; it is not surprising to find that under strong fields the system behaves as if it were a two-dimensional isotropic oscillator. In Appendix G we discuss a somewhat different approach to the strong-field solution which leads to the same results as those obtained here.

The presence of free rotations gives rise to a rather complicated pattern of energy levels superimposed upon the equally spaced levels of hindered rotations. It is interesting to note that by changing the quantum numbers K and M such that $|K-M|$ remains the same the symmetric molecule can undergo relatively small amounts of energy exchange. Physically this is to be expected since the rotational frequency about the axis of symmetry can be altered without affecting the relative orientation of $\underline{\mu}$ and $\underline{E}$. Since there is no rotation about the $\underline{e}_3$ axis in linear molecules this type of low-energy transitions is not possible as can be observed in (5.22).

The strong-field solutions which we have obtained represent a meaningful description of rotations of polar molecules whenever λ is sufficiently large so the use of small-angle approximation is justified. However, not all solutions are admissible since

$$\langle \theta^2 \rangle_{\varsigma K M} = \frac{1}{\eta}(2\varsigma + |K-M| + 1) , \tag{5.23}$$

and there will be values of ς and $|K-M|$ for which $\langle \theta^2 \rangle_{\varsigma K M}$ is no longer small. The physical breakdown of the model occurs when the energy available for rotation is so large that the effect of the electric field becomes negligible. Such a situation may be achieved by increasing the system temperature to the extent that the molecules can no longer "feel" the influence of the potential. In this limit one would expect the molecules to again resume completely free rotations. Unfortunately, the use of small-angle approximation at the outset prevents the dynamical behavior during this transition to be examined in the present formulation.*

The description of hindered rotations has not been satisfactorily generalized to the case of asymmetric molecule. We have considered the method of orthogonal transformation employed by Wang[44] in treating the free asymmetrical top and have found that the terms arising from the asymmetry [terms proportional to b in Eq. (D.5)] couple all states of the symmetric molecule. Hence numerical methods are required to diagonalize the resulting infinite matrix. On the other hand, we have observed that the energies of hindered rotation for symmetric and linear molecules are of the same form. Then it may be argued that in cases of strong coupling the symmetric molecule provides a reasonable first approximation to the asymmetrical molecule. The supposition that hindered

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*The use of a temperature-dependent field offers an interesting possible modification of the model through which a high-temperature limit may be derived.

rotations are not sensitive to system symmetries will be tested in a specific calculation of water to be discussed in the next chapter.

THE THERMAL AVERAGE

Recently Nelkin[23] has treated hindered rotations in water by means of an oscillator whose frequency was taken directly from neutron experiment and whose mass was an adjusted parameter fitted to the free-atom cross section in the Sachs-Teller mass tensor approximation. The reduction of rotations in a potential field to torsional oscillations has just been explicitly derived and in this respect it is possible to justify Nelkin's approach. The model proposed in this investigation provides a reasonably simple but realistic description of rotations of polar molecules in the liquid or even solid state, and is suitable for use in studying neutron scattering. We shall follow essentially the same approach developed in Chapter IV in evaluating the thermal average. It will be seen that the main features of Nelkin's calculation are contained in the present results although the corresponding expressions for the intensity of the scattering are markedly different. Moreover, the present treatment allows the effects of free rotations to be included in the general analysis.

We consider first the matrix element appropriate to neutron scattering by a single symmetric molecule,

$$\begin{aligned} \langle \alpha\alpha' ; \varsigma K M \rangle &= \langle \varsigma K M | e^{itH'_{SR}} e^{i\underline{K}\cdot\underline{b}_\alpha} e^{-itH'_{SR}} e^{-i\underline{K}\cdot\underline{b}_{\alpha'}} | \varsigma K M \rangle \\ &= \sum_{\varsigma' K' M'} Q \, e^{it(E_{\varsigma K M} - E_{\varsigma' K' M'})} \quad , \end{aligned} \tag{5.24}$$

where
$$Q = \langle \rho K M | e^{i\underline{k}\cdot\underline{b}_\alpha} | \rho' K' M' \rangle \langle \rho' K' M' | e^{-i\underline{k}\cdot\underline{b}_{\alpha'}} | \rho K M \rangle . \qquad (5.25)$$

The expansion (4.35) now gives

$$e^{i\underline{k}\cdot\underline{b}} = 4\pi \sum_{\ell k m \mu} i^\ell j_\ell(kb) Y_\ell^{k*}(\hat{\underline{b}}') Y_\ell^{\mu}(\hat{\underline{k}}) D^\ell_{-m,-k}(\psi\theta\varphi) D^\ell_{-\mu,-m}(\alpha\beta\gamma) , \qquad (5.26)$$

where under the transformation of successive rotations the spherical harmonic $Y_\ell^k(\hat{\underline{k}}')$ whose arguments are measured in the $\underline{e}_i'$ system is expressed as a linear combination of $Y_\ell^\mu(\hat{\underline{k}}^0)$ with components of $\hat{\underline{k}}^0$ measured in the laboratory or $\underline{e}_i^0$ system. The orientation of the space of $\underline{e}_i$ axes with respect to the laboratory system is specified by the Eulerian angles $(\alpha\beta\gamma)$. The laboratory axes are introduced because the direction of $\underline{E}$, which is along $\underline{e}_3$, must be averaged over all possible directions. By means of the orthogonality integral (4.39),

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

and the relation

$$\sum_\mu Y_\ell^\mu(\hat{\underline{k}}^0) Y_\ell^{\mu *}(\hat{\underline{k}}^0) = \frac{2\ell+1}{4\pi} ,$$

we obtain an expression for Q averaged over all the random directions of $\underline{E}$,

$$Q = (4\pi)^2 \sum_{\ell m k k'} j_\ell(kb_\alpha) j_\ell(kb_{\alpha'}) Y_\ell^{k*}(\hat{\underline{b}}_\alpha') Y_\ell^{k'}(\hat{\underline{b}}_{\alpha'}') \langle \rho K M | D^\ell_{-m,-k} | \rho' K' M' \rangle \langle \rho' K' M' | D^{\ell *}_{-m,-k'} | \rho K M \rangle . \qquad (5.27)$$

The indicated matrix elements can be reduced in view of (5.18),

$$\langle \rho K M | D^\ell_{-m,-k} | \rho' K' M' \rangle = (2\pi)^2 N_{\rho K M} N_{\rho' K' M'} \delta_{M,M'+m} \delta_{K,K'+k} F , \qquad (5.28)$$

$$\langle s'K'M'|D^{l*}_{-m,-k}|sKM\rangle = (2\pi)^2 N_{sKM} N_{s'K'M'} \delta_{M',M-m}\delta_{K',K-k'} F \,, \tag{5.29}$$

where normalization constant N_{sKM} is given by (5.20) and integral F is defined by

$$F = \frac{1}{2\eta}\int_0^\infty dx\, x^{\frac{|K-M|+|K'-M'|}{2}} e^{-x} L_s^{|K-M|} L_{s'}^{|K'-M'|} d^l_{-m,-k} \,, \tag{5.30}$$

with $\eta = \left(\frac{\lambda}{2B}\right)^{1/2}$. It is seen that for fixed K and K' the product of the two matrix elements requires k = k'. Thus

$$Q = 64\pi^5 N^2_{sKM} \sum_{lmk} j_l(K\underline{b}_\alpha) j_l(K\underline{b}_{\alpha'}) Y_l^{k*}(\hat{\underline{b}}'_\alpha) Y_l^k(\hat{\underline{b}}'_{\alpha'}) N^2_{s'K'M'} F^2 \,. \tag{5.31}$$

In the integral F the matrix element $d^l_{-m,-k}$ is according to (4.19),

$$d^l_{-m,-k} = G^l_{-m,-k} \sum_s g^l_{-m,-k}(s) \left(\cos\frac{\theta}{2}\right)^{2l-k+m+2s} \left(-\sin\frac{\theta}{2}\right)^{k-m+2s} \,, \tag{5.32}$$

where

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

$$g^l_{-m,-k}(s) = (-)^s \left[(l+m-s)!\,(l-k-s)!\,(s+k-m)!\,s!\right]^{-1} .$$

In keeping with the small-angle approximation used to obtain the rotator wave function we may write

$$d^l_{-m,-k}(\theta) \cong (-)^{m-k} G^l_{mk} \sum_s g^l_{-m,-k}(s) \left(\frac{\theta}{2}\right)^{k-m+2s} e^{-\frac{\theta^2}{4}(2l-k+m-2s)} \,, \tag{5.33}$$

which leads to an explicit expression for F,

$$F \cong \frac{(-)^{m-k}}{2\eta} G^l_{mk} \sum_s g^l_{-m,-k}(s) \left(\frac{1}{4\eta}\right)^{s+\frac{k-m}{2}} S_{ss'}(p,q;\mu) \,, \tag{5.34}$$

$$S_{\varsigma\varsigma'}(pjq;\mu) = \int_0^\infty dx\, x^{p}\, e^{-(\mu+1)x}\, L_{\varsigma}^{p-j}\, L_{\varsigma'}^{p-q}\ , \qquad (5.35)$$

$$\mu = \frac{1}{4\eta}(2l+m-k-2s)$$

$$\begin{aligned} 2p &= |K-M| + |K-M+m-k| + 2s - m + k \\ 2j &= |K-M+m-k| - |K-M| + 2s - m + k \qquad (5.36) \\ 2q &= |K-M| - |K-M+m-k| + 2s - m + k\ . \end{aligned}$$

We note that p, j, q are always positive integers or zero. The integral S can be evaluated in terms of the generating function of the associated Laguerre polynomial (see Appendix F),

$$\begin{aligned} S_{\varsigma\varsigma'}(pjq;\mu) &= (-)^{\varsigma+\varsigma'}(\varsigma+p-j)!\,(\varsigma'+p-q)! \qquad (5.37) \\ &(\times) \sum_{\sigma} \sum_{d}^{\sigma} (-)^{\sigma+d} \frac{\mu^{\sigma-d}(p+\sigma)!\,(j+\sigma-d)!\,(q+\sigma-d)!}{d!\,(\sigma-d)!\,(\varsigma'-d)!\,(\varsigma-d)!\,(j+\sigma-\varsigma)!\,(q+\sigma-\varsigma')!}\ , \end{aligned}$$

where the summations are such that arguments of the factorials in the denominator must never be negative. For a given ς, j, q, and p Eq. (5.37) can be used to derive the correponding selection rules for ς'.

The Eqs. (5.24), (5.31), (5.34), and (5.37) comprise a formal description of neutron scattering by a hindered symmetric rotator. As with the earlier case of free rotators, the present approach results in an explicit summation of all possible transitions, and consequently requires considerable reductions before a particular process can be investigated in detail. It is noted that in (5.34) a natural and convenient expression for F can be developed as a power series in $\left(\frac{1}{4\eta}\right)^{1/2}$, where $\eta = \left(\frac{\lambda}{2B}\right)^{1/2} \gg 1$.

The leading terms are

$$F = F_0 + \left(\tfrac{1}{4\eta}\right)^{1/2} F_1 + \tfrac{1}{4\eta} F_2 + O\left[\left(\tfrac{1}{4\eta}\right)^{3/2}\right], \qquad (5.38)$$

$$F_0 = \delta_{Mk} \int dx\, x^{|K-M|} e^{-x} L_s^{|K-M|} L_{s'}^{|K-M|},$$

$$F_1 = -\delta_{M,k\pm1}\left[(l\mp k)(l\pm k+1)\right]^{1/2} \int dx\, x^{\frac{|K-M|+|K-M\pm1|+1}{2}} e^{-x} L_s^{|K-M|} L_{s'}^{|K-M\pm1|},$$

$$F_2 = -\delta_{Mk}(l^2-k^2+l) \int dx\, x^{|K-M|+1} e^{-x} L_s^{|K-M|} L_{s'}^{|K-M|}.$$

The integrals in F_i are special cases of (5.37) with $\mu=0$, they are of the form

$$S_{ss'}(pjq) = \int_0^\infty dx\, x^p e^{-x} L_s^{p-j} L_{s'}^{p-q}$$

$$= (-)^{s+s'} (s+p-j)!\,(s'+p-q)!\,j!\,q! \qquad (5.39)$$

$$(x) \sum_\sigma \frac{(p+\sigma)!}{\sigma!\,(s-\sigma)!\,(s'-\sigma)!\,(j+\sigma-s)!\,(q+\sigma-s')!}$$

in which $\mathrm{Max}\binom{s-j-1}{s'-q-1} < \sigma < \min\binom{s+1}{s'+1}$. If the condition on σ is not satisfied then the integral is zero, indicating all transitions are forbidden.

Since F appears in the thermal average as F^2 it will be sufficient for most cases to retain only the first two terms in (5.38). By ignoring the term $\sim \frac{1}{4\eta}$ in F we are effectively neglecting a correction to F_0, which represents elastic scattering, of order $\frac{1}{4\eta}$ and inelastic terms of order $\left(\frac{1}{4\eta}\right)^2$ which are different from those given by F_1. In order to exhibit the nature of the energy transfer with hindered modes of rotation we shall, for the present, ignore free-rotation energies in E_{sKM}. The matrix element (5.24) can now be written as

$$\langle\alpha\alpha';\varsigma KM\rangle = \langle\alpha\alpha';\varsigma\tau\rangle$$

$$= 4\pi\sum_{\ell k} j_\ell(Kb_\alpha)\, j_\ell(Kb_{\alpha'})\, Y_\ell^{k*}(\hat{b}'_\alpha)\, Y_\ell^{k}(\hat{b}'_{\alpha'})\, W(\varsigma,\tau,t), \tag{5.40}$$

where

$$W(\varsigma,\tau,t) = \frac{\varsigma!}{[(\varsigma+\bar\tau)!]^3}\sum_{\varsigma' m}\frac{\varsigma'!}{[(\varsigma'+|\tau-k+m|)!]^3}(2\eta F)^2\, e^{it(E_{\varsigma\bar\tau}-E_{\varsigma'|\tau-k+m|})}, \tag{5.41}$$

$$(2\eta F)^2 = \delta_{mk}\,\mathcal{S}^2_{\varsigma\varsigma'}(\bar\tau 00) \tag{5.42}$$

$$+\delta_{m,k\pm1}\frac{1}{4\eta}(\ell\mp k)(\ell\pm k+1)\,\mathcal{S}^2_{\varsigma\varsigma'}\left(\frac{\bar\tau+|\tau\pm1|+1}{2},\frac{|\tau\pm1|+1-\bar\tau}{2},\frac{\bar\tau+1-|\tau\pm1|}{2}\right).$$

In the above notation $\tau = K-M$, $\bar\tau = |\tau|$, and in (5.42) the second term is to be regarded as a sum of two terms corresponding to upper and lower signs respectively. The energy becomes $E_{\varsigma\bar\tau} = \sqrt{2\lambda B(2\varsigma+\bar\tau+1)} - \lambda$ as a result of ignoring free rotations, and the matrix element is only a function of τ instead of K and M separately. The simplification thus resulted is more apparent in performing average over initial states, for we have

$$\langle\alpha\alpha'\rangle_T = \Big(\sum_{\varsigma KM} e^{-\beta E_{\varsigma KM}}\Big)^{-1}\sum_{\varsigma KM}\langle\alpha\alpha';\varsigma KM\rangle e^{-\beta E_{\varsigma KM}} = \Gamma\sum_{\varsigma\tau}\langle\alpha\alpha';\varsigma\tau\rangle e^{-\beta E_{\varsigma\bar\tau}}, \tag{5.43}$$

where $\Gamma = \Big(\sum_{\varsigma\tau} e^{-\beta E_{\varsigma\bar\tau}}\Big)^{-1}$ and

$$\langle\alpha\alpha';\varsigma,+\bar\tau\rangle + \langle\alpha\alpha';\varsigma,-\bar\tau\rangle = \tag{5.44}$$

$$4\pi\sum_{\ell k} j_\ell(Kb_\alpha)\, j_\ell(Kb_{\alpha'})\, Y_\ell^{k*}(\hat{b}'_\alpha)\, Y_\ell^{k}(\hat{b}'_{\alpha'})\Big\{W(\varsigma,\bar\tau,t) + W(\varsigma,-\bar\tau,t)\Big\}.$$

The calculation of $W(\varsigma,\pm\bar\tau,t)$ requires explicit determination of the integrals $\mathcal{S}^2_{\varsigma\varsigma'}(pjq)$ and associated selection rules for ς'. After a series of straightforward manipulations with (5.42) and (5.39) we find

$$W(\varsigma,0,t) = 1 + \frac{2\left[l(l+1)-k^2\right]}{4\eta}\left\{\varsigma e^{it\sqrt{2\lambda B'}} + (\varsigma+1)\, e^{-it\sqrt{2\lambda B'}}\right\}, \qquad (5.45)$$

$$W(\varsigma,\pm\bar{\kappa},t) = 1 + \frac{(l\pm k)(l\mp k+1)}{4\eta}\left\{(\varsigma+\bar{\kappa})\, e^{it\sqrt{2\lambda B'}} + (\varsigma+1)\, e^{-it\sqrt{2\lambda B'}}\right\} \qquad (5.46)$$

$$+ \frac{(l\mp k)(l\pm k+1)}{4\eta}\left\{\varsigma e^{it\sqrt{2\lambda B'}} + (\varsigma+\bar{\kappa}+1)\, e^{-it\sqrt{2\lambda B'}}\right\}.$$

Thus for $\bar{\kappa} \neq 0$,

$$W(\varsigma,\bar{\kappa},t) + W(\varsigma,-\bar{\kappa},t) = 2\left\{1 + \frac{\left[l(l+1)-k^2\right]}{4\eta}\left[(2\varsigma+\bar{\kappa})\, e^{it\sqrt{2\lambda B'}} + (2\varsigma+\bar{\kappa}+2)\, e^{-it\sqrt{2\lambda B'}}\right]\right\}. \qquad (5.47)$$

The indicated summations over ς and $\bar{\kappa}$ can now be carried out,

$$\langle 1 \rangle \equiv \sum_{\varsigma=0}^{\infty}\sum_{\bar{\kappa}=-\infty}^{\infty} e^{-\beta E_{\varsigma\bar{\kappa}}} = (1-e^{-\nu})^{-2},$$

$$\langle 2\varsigma+\bar{\kappa} \rangle = \frac{2e^{-\nu}(1+e^{-\nu})}{(1-e^{-2\nu})(1-e^{-\nu})^2}, \quad \langle 2\varsigma+\bar{\kappa}+2 \rangle = \frac{2(1+e^{-\nu})}{(1-e^{-2\nu})(1-e^{-\nu})^2}, \qquad (5.48)$$

where $\nu = \beta\sqrt{2\lambda B'}$. The thermal average becomes simply

$$\langle \alpha\alpha' \rangle_T = 4\pi \sum_l j_l(\kappa b_\alpha)\, j_l(\kappa b_{\alpha'}) \sum_{k=-l}^{l} Y_l^{k*}(\hat{b}'_\alpha)\, Y_l^{k}(\hat{b}'_{\alpha'}) \qquad (5.49)$$

$$(\times)\left\{1 + \frac{(1+e^{-\nu})\left[l(l+1)-k^2\right]}{2\eta(1-e^{-2\nu})}\left(e^{-\nu} e^{it\sqrt{2\lambda B'}} + e^{-it\sqrt{2\lambda B'}}\right)\right\}.$$

In arriving at (5.49) average over initial states has been performed using all possible states. However, this procedure is not entirely consistent with the rotator model since large ς and ζ values are not allowed by virtue of (5.23). For cases with $\nu \gtrsim 1$ we anticipate no significant error due to the rapid attenuation provided by the Boltzmann factor. If only a smaller set of quantum states are to be used in the average the appropriate partial sums may still be performed without difficulty.

The first term in $\langle \alpha\alpha' \rangle_T$ represents the contribution to the cross section from elastic scattering. It is in fact expressible as $j_0(\kappa|\underline{b}_\alpha - \underline{b}_{\alpha'}|)$, the result obtained in the static approximation for free molecules. As to be expected, elastic processes only depend upon system symmetries and is not influenced by dynamical details of a particular model. The time-dependent terms in (5.49) correspond to "one-quantum" transitions in which neutron energy is increased and decreased respectively by an amount $\sqrt{2\lambda B'}$, the spacing of hindered rotation levels. This relatively large energy transfer may be interpreted as the hindered rotation peak similar to those observed in scattering from water and ammonium halides. The same nature of inelasticity can be obtained by treating the rotator as an ordinary oscillator with frequency $\hbar^{-1}\sqrt{2\lambda B'}$ and in this respect the nature of approximation in Nelkin's model for water is demonstrated. Higher-order inelastic scatterings do not appear in the thermal average because terms of order $\frac{1}{4\nu}$ and higher have been neglected in computing F. It can be readily shown that the term F_2 will give rise to "two-quanta" transitions whose intensity is lower by a factor of $\frac{1}{4\nu}$ compared to the "one-quantum" processes.

The index ℓ plays essentially the same role as in the free-rotator problem since identical expansions have been employed. Inelastic scattering is seen to be possible only if ℓ is non-zero. Because each term in (5.49) represents all the contributions to that particular process, all values of ℓ greater than or equal to one will contribute to the "one-quantum" transitions.

It is observed that elastic scattering is temperature independent. The absence of a Debye-Waller factor is a direct consequence of the assumption of rigid molecular bonds. Nevertheless, temperature effects introduced by the averaging over initial states indicate that neutron energy loss at finite temperatures is always more probable than energy gain, the latter process is completely restricted at T = 0. In the limit of high temperatures the intensity of both processes varies like ν^{-1} due to the fact that many more states are able to participate in inelastic scattering. The equal probability for scattering up or down suggests in these results a certain degree of classical phenomenon. As noted previously, the high-temperature limit in which free rotations are obtained is not available in the present model by virtue of the small-angle approximation.

Corresponding result for linear molecules may again be derived directly from (5.49). By noting that $Y_\ell^k(0\psi) = \delta_{k0}\sqrt{\frac{2\ell+1}{4\pi}}$ we have

$$\begin{aligned}\langle\alpha\alpha'\rangle_T &= \sum_\ell (2\ell+1)(2\delta_{\alpha\alpha'}-1)^\ell j_\ell(\kappa b_\alpha) j_\ell(\kappa b_{\alpha'}) \\ &(\mathrm{x})\left\{1 + \frac{(1+e^{-\nu})\ell(\ell+1)}{2\eta(1-e^{-2\nu})}\left(e^{-\nu} e^{it\sqrt{2\lambda B}} + e^{-it\sqrt{2\lambda B}}\right)\right\}.\end{aligned} \qquad (5.50)$$

The thermal averages given by (5.49) and (5.50) are valid for any incident neutron energy. In the case of very low energy further simplification is available. The small arguments expression for $j_\ell(x)$ mentioned in Chapter IV leads to expressions in power series of $K_0 b$. For instance, for linear molecules we would find

$$\langle\alpha\alpha'\rangle_T \cong \sum_{\ell} \frac{(2\ell+1)(2\delta_{\alpha\alpha'}-1)^{\ell}(K_0 b_\alpha)^{\ell}(K_0 b_{\alpha'})^{\ell}}{[(2\ell+1)!!]^2}\left[1-\frac{(K_0 b_\alpha)^2}{2(2\ell+3)}\right]\left[1-\frac{(K_0 b_{\alpha'})^2}{2(2\ell+3)}\right]$$

$$(\times)\left\{1+\frac{(1+e^{-\nu})\ell(\ell+1)}{2\eta(1-e^{-2\nu})}\left(e^{-\nu}e^{it\sqrt{2\lambda B}}+e^{-it\sqrt{2\lambda B}}\right)\right\}.$$

An appropriate high energy limit will be discussed separately in the following section.

For scattering from different molecules, we need to evaluate

$$\langle\alpha\alpha' ; \xi KM\rangle_0 = \langle\xi KM|\, e^{i\underline{K}_0\cdot\underline{b}_\alpha}\,|\xi KM\rangle\langle\xi KM|\, e^{-i\underline{K}_0\cdot\underline{b}_{\alpha'}}\,|\xi KM\rangle .$$

We shall be content with averaging the product over orientations of the electric field separately. This is equivalent to assuming no directional correlation from one molecule to another. Thus

$$\langle\alpha\alpha' ; \xi KM\rangle_0 = j_0(K_0 b_\alpha)\, j_0(K_0 b_{\alpha'}) . \qquad (5.51)$$

Again, as a consequence of the single-particle model, "outer" effects are purely elastic and independent of initial state of the molecule.

Thus far we have not considered the effects of free rotations. It is to be expected that these effects will not significantly alter the essential features of the preceding results. On the other hand, there are two interesting aspects associated with the results which take into account of free rotation energies, namely, that there will be inelastic scatterings associated with low-energy transfer and that many transitions involving energies of order $\sqrt{2\lambda B'}$ will be allowed. A detailed consideration of these effects is discussed in Appendix H, we shall mention here some of the conclusions. The selection rules for ξ' is independent of the form of $E_{\xi KM}$, therefore only the case m = k, which previously gave rise to elastic scattering, needs to be examined for transitions involving only the terms proportional to B. The cases m = k±1 will contribute to a number of transitions involving an exchange of $\pm\sqrt{2\lambda B'}$ and some free-rotation energies; because of the dependence of $E_{\xi KM}$ on K^2, M^2, and KM a rich spectrum of inelasticities is produced. The resulting energy distribution will thus exhibit certain peaks in the low energy region corresponding to excitations of free-rotation levels and the somewhat broadened hindered rotation peaks centered roughly about $\epsilon_f = \epsilon_i \pm \sqrt{2\lambda B'}$. For linear molecules the low-energy peaks do not appear as previously noted.

A HIGH-ENERGY APPROXIMATION

The formalism in the preceding section becomes cumbersome whenever the incident neutron energy is high enough to induce a great number of transitions. In this case the quantity of interest is usually the angular differential cross section for which the mass-ratio expansion developed by Zemach and Glauber[1] can be applied. This method, previously discussed only in connection with free molecules,[1,36] can be used with the hindered rotator model. We will consider the application to linear molecules and show that for very high energy neutrons the distinction between hindered and free rotations vanishes, a limit one would expect on purely physical grounds.

We return to the matrix element for direct scattering by a linear molecule in a given initial state,

$$\langle \alpha\alpha' ; \xi M\rangle = \langle \xi M | e^{itH} e^{-itH'} | \xi M\rangle , \tag{5.52}$$

where $H = \frac{\hbar^2 L^2}{2\mathcal{M}b^2} - \underline{\mathcal{M}}\cdot\underline{E}$, with $\underline{I} = \mathcal{M}b^2$, and we have defined $H' = e^{i\underline{K}\cdot\underline{b}} H e^{-i\underline{K}\cdot\underline{b}}$. According to the Lie expansion

$$e^{S} Q e^{-S} = Q + [S,Q] + \tfrac{1}{2}[S,[S,Q]] + \cdots , \tag{5.53}$$

we have

$$\underline{L}' = \underline{L} + (\underline{K}\times\underline{b}), \tag{5.54}$$

$$H' = H + \frac{\hbar^2}{2\mathcal{M}b}\left[\underline{K}\cdot(\underline{b}\times\underline{L} - \underline{L}\times\underline{b}) + (\underline{K}\times\underline{b})^2\right]. \tag{5.55}$$

In arriving at $\underline{L}'$ the different components may be taken with respect to either body or space axes; in the former case the commutators involve components of L_i and K_i, and will have a minus sign associated with the commutation relations.[36,47] For the moment we shall proceed formally. Since H is diagonal in the representation $|\xi M\rangle$, Eq. (5.52) can be written as

$$\langle \alpha\alpha ; \xi M\rangle = \langle \xi M | e^{-it(H' - E_{\xi M})} | \xi M\rangle , \tag{5.56}$$

where

$$H' - E_{\xi M} = (H - E_{\xi M}) - \frac{i\hbar^2 K}{\mathcal{M} b}\beta + \frac{\hbar^2 K^2}{2\mathcal{M}}\gamma \;,$$

$$\beta = \underline{K}\cdot(\underline{b} + i\,\underline{b}\times\underline{L})/Kb$$

$$\gamma = (\underline{K}\times\underline{b})^2/(Kb)^2$$

For the purpose of present discussion we shall ignore the translational and vibrational degrees of freedom of the molecule. Then for a given initial state the contribution to the cross section from direct scattering is

$$\sigma_d(\epsilon_i, \Omega, \epsilon_f) = \frac{a^2 k_f}{2\pi k_i}\int dt \langle \alpha\alpha\, ; \xi M\rangle\, e^{-i\epsilon t} \;, \tag{5.57}$$

where the scattering length is denoted as a. Now consider the Taylor expansion

$$\langle \alpha\alpha\, ; \xi M\rangle = \sum_{n=0}^{\infty} c_n \left(\frac{it}{\mathcal{M}}\right)^n \;, \tag{5.58}$$

which when inserted into (5.57) gives

$$\sigma_d(\epsilon_i, \Omega, \epsilon_f) = \frac{a^2 k_f}{k_i}\sum_n c_n \left(-\frac{1}{\mathcal{M}}\right)^n \left(\frac{\partial}{\partial\epsilon}\right)^n \delta(\epsilon) \;. \tag{5.59}$$

The angular distribution is obtained by integrating over all energy transfer,

$$\begin{aligned} \sigma_d(\theta) &= \int \sigma_d(\epsilon_i, \Omega, \epsilon_f)\, d\epsilon \\ &= \frac{a^2}{k_i}\sum_n \left(\frac{1}{\mathcal{M}}\right)\left(\frac{\partial}{\partial\epsilon}\right)^n (k_f c_n)_{\epsilon=0} \\ &= \frac{a^2}{k_i}\sum_n \left(\frac{m}{\mathcal{M}}\right)^n \left(\frac{1}{\hbar^2 k_f}\frac{\partial}{\partial k_f}\right)^n (k_f c_n)_{k_f=k_i} \;. \end{aligned} \tag{5.60}$$

Thus the time expansion (5.58) results in an expression in power series of the mass ratio for the angular differential cross section.

In order to determine the coefficients of the time expansion we examine (5.56) in the form

$$e^{-it(H'-E_{SM})} = 1 - \left(\frac{it}{M}\right)\left(\frac{\hbar^2\kappa^2\gamma}{2} - \frac{i\hbar^2\kappa\beta}{b}\right) \tag{5.61}$$
$$+ \frac{\hbar^2}{2}\left(\frac{it}{M}\right)^2\left\{(H-E_{SM})M\left(\frac{\kappa^2\gamma}{2} - \frac{i\kappa\beta}{b}\right) + \left(\frac{\kappa^2\gamma}{2} - \frac{i\kappa\beta}{b}\right)\right\}$$
$$+ \cdots ,$$

where terms which obviously have zero expectation values have been omitted. For the expectation values of these terms we introduce the hindered rotator model in which three vectors need to be specified. As before the neutron momentum transfer $\underline{\kappa}$ will be chosen along the laboratory-z axis, the electric field $\underline{E}$ along the space-z axis, and dipole moment $\underline{\mu}$ along the molecular axis. Since $\underline{E}$ does not appear in (5.61) the average over all electric field orientations may be conveniently replaced by average over directions of $\underline{\kappa}$. Moreover, among the products of various components of $\underline{\kappa}$ and $\underline{b}$ it is not necessary to rotate the momentum transfer vector back to the laboratory system for the averaging, the same results are obtained by integrating these components of $\underline{\kappa}$ with respect to a set of axes of which the z axis is along $\underline{b}$. One readily finds

$$\langle\beta\rangle_{AV.} = \langle\gamma\beta\rangle_{AV} = \langle\beta\gamma\rangle_{AV} = 0\,, \quad \langle\gamma\rangle_{AV} = \frac{2}{3}\,, \quad \langle\gamma^2\rangle_{AV} = \frac{8}{15}$$
$$\langle\beta^2\rangle_{AV} = \frac{1}{3}\left\{1 - \sum_{j,k=1}^{3}\hat{b}_jL_k(\hat{b}_jL_k - \hat{b}_kL_j)\right\}, \tag{5.62}$$

where $\langle\ \rangle_{AV}$ denotes the average over electric field orientations. To order t^2 the only expectation value in (5.61) that requires further attention is the term $\langle \beta^2 \rangle_{AV}$, for which explicit representation of the angular momentum operators P_i are given in Appendix D. In this case,

$$L_1 = i\left(\cot\theta\cos\psi\frac{\partial}{\partial\psi} + \sin\psi\frac{\partial}{\partial\theta}\right),$$

$$L_2 = i\left(\cot\theta\sin\psi\frac{\partial}{\partial\psi} - \cos\psi\frac{\partial}{\partial\theta}\right),$$

$$L_3 = -i\frac{\partial}{\partial\psi}\,.$$

Of the nine terms in the summation only six have to be evaluated. After some manipulation it is found that

$$\langle \beta^2 \rangle_{AV} = \frac{1}{3}\left\{1 + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\psi^2}\right\}. \qquad (5.63)$$

The last two terms in the bracket are seen to be precisely the kinetic energy operator so the expectation of $\langle \beta^2 \rangle_{AV}$ can be readily computed. The matrix element thus has the following time expansion

$$\langle \alpha\alpha' ; \varsigma M \rangle = 1 - \left(\frac{it}{\mathcal{M}}\right)\frac{\hbar^2 K^2}{3} + \left(\frac{it}{\mathcal{M}}\right)^2 \hbar^4 \left\{\frac{K^4}{15} + \frac{K^2}{6b^2}\left[\left(\frac{2\lambda}{B}\right)^{1/2}(2\varsigma + |M| + 1) + \frac{M^2}{3} - 1\right]\right\}. \qquad (5.64)$$

For comparison we quote the free molecule result derived by Zemach and Glauber,[1]

$$\langle \alpha\alpha' ; JM \rangle = 1 - \left(\frac{it}{\mathcal{M}}\right)\frac{\hbar^2 K^2}{3} + \left(\frac{it}{\mathcal{M}}\right)^2 \hbar^4 \left\{\frac{K^4}{15} + \frac{K^2}{6b^2}(J^2 + J + 1)\right\}. \qquad (5.65)$$

Since J(J+1) is the energy of a free linear molecule there exists complete analogy between these two results except for the somewhat puzzling reversal of sign of the last term. However, both terms in $\left(\frac{m}{M}\right)^2\frac{\hbar^4 k^2}{6b^2}$ are always positive even in the ground state.

The coefficients of $\left(\frac{m}{M}\right)^n$ in (5.64) are the required C_n's. According to (5.60) the angular differential cross section for direct scattering by a hindered rotator in the eigenstate $|\varsigma M\rangle$ becomes

$$a^{-2}\sigma_d(\theta) = 1-\left(\frac{m}{M}\right)\left(\frac{4}{3}-\frac{4}{3}\cos\theta\right) + \left(\frac{m}{M}\right)^2\left\{(1-\cos\theta)\left[\frac{4}{3}-\frac{4}{5}\cos\theta\right]+\frac{1}{3}\left[\left(\frac{2\lambda}{B}\right)^{1/2}(2\varsigma+|M|+1)+\frac{M^2}{3}-1\right](k_ib)^{-2}\right\}. \quad (5.66)$$

This result is useful for the study of angular distributions at relatively high incident energy $(k_ib \gtrsim 1)$ and small mass ratio. The "inner" scattering can be similarly treated. In this result dependence on system dynamics first appears in the correction term of order $\left(\frac{m}{M}\right)^2(k_ib)^{-2}$. Therefore at large energies effects of the hindrance become increasingly insignificant and the scattering is expected to be insensitive to the choice of models.

CHAPTER VI

SLOW-NEUTRON SCATTERING BY DIATOMIC LIQUIDS

We consider specific calculations based on the dynamical models developed in Chapters III and V. It is our main purpose in this chapter to determine what aspects of the differential cross section are sensitive to details of molecular translations and rotations, and to what extend does the incident neutron spectrum influence the final energy distribution in studying hindrances in molecular motions. The calculations are made for diatomic polar liquids since it is the simplest system that embodies all the essential features of molecular dynamics in the present description.

The differential cross section $\sigma(\epsilon_i, \theta, \epsilon_f)$ is computed for liquid HCl at 188°K. As there are no reported measurements using any diatomic polar liquid the results obtained here can well serve as a guide for future experiments.

Because water is an important system from the standpoint of liquid theory as well as neutron moderation in nuclear reactors it has received considerable experimental attention as previously mentioned. In this investigation the differential cross section for water is computed in an approximation where the asymmetric molecule is replaced by a diatomic molecule of equivalent mass and permanent electric dipole moment. The results are then compared with the measurements of Brockhouse and Nelkin's calculation.

ENERGY AND ANGULAR DIFFERENTIAL CROSS SECTION FOR POLAR DIATOMIC MOLECULES

According to the formalism derived in Chapter II the differential cross section $\sigma(\epsilon_i, \theta, \epsilon_f)$ (the cross section is azimthally symmetric) is determined once the thermal averages appropriate to the various degrees of freedom are obtained. When the center-of-mass degrees of freedom are treated by the methods of Chapter III the translational thermal averages are given by Eqs. (3.25) and (3.26). By ignoring the vibration-rotation coupling it is shown in Appendix I that the description of vibrational degree of freedom is that appropriate to an oscillator, but on account of the non-commutation between H_R and $\underline{C}_{\ell\alpha}$ vibrational and rotational thermal averages are still not separable. The thermal average for the internal degrees of freedom, in the case of $\ell = \ell'$, can be taken from Eq. (2.33)

$$\langle \chi^{I}_{\substack{\ell\ell \\ \alpha\alpha'}} \rangle_T = \sum_{SM} P_{SM} \langle SM| e^{i\underline{K}_\ell\cdot\underline{b}_\alpha(t)} V_{\alpha\alpha'} e^{-i\underline{K}_\ell\cdot\underline{b}_{\alpha'}} |SM\rangle , \qquad (6.1)$$

$$V_{\alpha\alpha'} = \sum_k P_k \langle k| e^{i\underline{K}_\ell\cdot\hat{\underline{b}}_\alpha(t)\rho_\alpha(t)} e^{-i\underline{K}_\ell\cdot\hat{\underline{b}}_{\alpha'}\rho_{\alpha'}} |k\rangle , \qquad (6.2)$$

where

$$\hat{\underline{b}}_\alpha(t) = e^{itH_R}\, \hat{\underline{b}}_\alpha\, e^{-itH_R} \; ; \quad \rho_\alpha(t) = e^{itH_V}\, \rho_\alpha\, e^{-itH_V}$$

The eigenstates $|k\rangle$ are just oscillator eigenstates, so

$$V_{\alpha\alpha'} = e^{-\frac{\hbar}{4\tau\Omega}\left[\underline{\kappa}\cdot h_\alpha \underline{b}_\alpha(t)\right]^2 \coth\frac{\beta\hbar\Omega}{2}}$$

$$(x) \sum_{n=-\infty}^{\infty} e^{n\left(i\hbar\Omega t - \frac{\beta\hbar\Omega}{2}\right)} I_n\left[\frac{\hbar\{\underline{\kappa}\cdot h_\alpha \hat{\underline{b}}_\alpha(t)\}\{\underline{\kappa}\cdot h_{\alpha'}\hat{\underline{b}}_{\alpha'}\}}{2\tau\Omega \sinh\frac{\beta\hbar\Omega}{2}}\right]$$

$$(x) \; e^{-\frac{\hbar}{4\tau\Omega}\left[\underline{\kappa}\cdot h_{\alpha'}\hat{\underline{b}}_{\alpha'}\right]^2 \coth\frac{\beta\hbar\Omega}{2}} \qquad (6.3)$$

,

where for diatomic molecules $\rho_\alpha = h_\alpha \rho$, $h_1 = \frac{M_2}{M_1+M_2}$ and $h_2 = \frac{M_1}{M_1+M_2}$. The internuclear vibrational frequency and reduced mass are denoted here as Ω and τ respectively. Note the ordering of time-dependent and time-independent operators, $\hat{\underline{b}}(t)$ and $\hat{\underline{b}}$, are respected. This expression for $V_{\alpha\alpha'}$ is to be inserted in (6.1) when averaging over-all molecular orientations. A formal method which is applicable when $\frac{\hbar\kappa^2}{2\tau\Omega}\coth\frac{\beta\hbar\Omega}{2} < 1$ is described in Appendix J.

Since the effect of rotation of axis of vibration on neutron scattering has been shown to be small[2] we shall proceed under the approximation that the effect can be ignored entirely in which case $[\underline{\kappa}\cdot\hat{\underline{b}}_\alpha(t)]^2$ and $(\underline{\kappa}\cdot\hat{\underline{b}}_{\alpha'})^2$ will be replaced by κ^2. Compared to the Krieger and Nelkin approach of averaging the exponent[2] the present approximation allows greater attenuation of the intensity of scattering due to vibrational motions. Thus

$$V_{\alpha\alpha'} = e^{-\frac{\hbar K_1^2}{4\mu\Omega}(h_\alpha^2+h_{\alpha'}^2)\coth\frac{\beta\hbar\Omega}{2}}$$

$$(\times)\sum_{n=-\infty}^{\infty} e^{n(i\hbar\Omega t - \frac{\beta\hbar\Omega}{2})} I_n\left(\frac{\hbar K_1^2 h_\alpha h_{\alpha'}}{2\mu\Omega\sinh\frac{\beta\hbar\Omega}{2}}\right) \qquad (6.4)$$

For the range of neutron energies $(\epsilon_i \sim 10^{-3} - 10^{-2}\ \mathrm{ev})$ and temperatures ($T \lesssim 373°K$) of interest excitations of vibrational levels are highly unlikely. We may then adopt the low-temperature limit and admit only elastic scattering,

$$V_{\alpha\alpha'} = e^{-\frac{\hbar K_1^2}{4\mu\Omega}(h_\alpha^2+h_{\alpha'}^2)} \qquad (6.5)$$

The effect of internuclear vibration is therefore characterized entirely by an exponential factor, and in this approximation the same results applies in the case of $l \neq l'$.

When the vibrational and rotational thermal averages are evaluated independently as we have done here, the formulae derived in Chapter V can be used directly. The thermal average (6.1) becomes

$$\langle \chi^{I}_{ll'\,\alpha\alpha'} \rangle_T = V_{\alpha\alpha'}\langle \alpha\alpha' \rangle_T \quad ; \; l = l' \qquad (6.6)$$

$$= V_{\alpha\alpha'}\, j_0(K_1 b_\alpha)\, j_0(K_1 b_{\alpha'}) \quad ; \; l \neq l' \qquad (6.7)$$

where $\langle \alpha\alpha' \rangle_T$ is given by (5.50). The appropriate thermal averages can then be inserted into the expression for the differential cross section (2.27). Performing the indicated integration we find

$$\sigma(\epsilon_i,\theta,\epsilon_f) = \left(\frac{\epsilon_f}{\epsilon_i}\right)^{1/2} e^{-DK_1^2} \sum_{\alpha\alpha'} (A_{l\alpha}A_{l\alpha'} + C_{l\alpha}C_{l\alpha'}S_{\alpha\alpha'})$$

$$(\times)\ e^{-\frac{\hbar K_1^2}{4\tau\Omega}(h_\alpha^2+h_{\alpha'}^2)} \sum_{l} (2l+1) j_l(K_1 b_\alpha) j_l(K_1 b_{\alpha'}) (2S_{\alpha\alpha'}-1)^l \sum_{n=-\infty}^{\infty} e^{-nz} I_n(PK_1^2)$$

$$(\times) \left\{ \delta(\epsilon - n\hbar\omega) + \frac{l(l+1)(1+e^{-\nu})}{2\eta(1-e^{-2\nu})} \left[\delta(\epsilon - n\hbar\omega - \sqrt{2\lambda B})\, e^{-\nu} + \delta(\epsilon - n\hbar\omega + \sqrt{2\lambda B}) \right] \right\}$$

$$+\ \delta(\epsilon)\, e^{-DK_1^2} \frac{1}{N} \sum_{ll'}{}' e^{i\underline{K}_1\cdot(\underline{x}_l - \underline{x}_{l'})}$$

$$(\times) \sum_{\alpha\alpha'} A_{l\alpha}A_{l'\alpha'} j_0(K_1 b_\alpha) j_0(K_1 b_{\alpha'})\, e^{-\frac{\hbar K_1^2}{4\tau\Omega}(h_\alpha^2+h_{\alpha'}^2)} \qquad (6.8)$$

The use of oscillator approximation for molecular translations results in discrete energy transfers as noted in Chapter III. The first term $(l=l')$ in (6.8) consists of contributions from direct $(\alpha=\alpha')$ and "inner" scatterings. The second term represents "outer" scattering $(l \neq l')$, and since it is purely elastic this term will not be considered in computing the energy distribution of scattered neutrons.

An alternative to the oscillator description of the center-of-mass is the description in which the molecules move in a square well (see

Appendix C). In the limit of very large well width or high temperature where it is justified to replace the summation over initial states by an integral the translational thermal average is that appropriate to gas molecules,[1]

$$\left\langle e^{i\underline{K}_1\cdot\underline{R}_\ell(t)}\, e^{-i\underline{K}_1\cdot\underline{R}_0}\right\rangle_T = e^{-it\frac{\hbar K_1^2}{2M}}\, e^{-\frac{(K_1 t)^2}{2M\beta}} , \qquad (6.9)$$

the "outer" scattering being negligible. The differential cross section corresponding to free translations is then readily derived,

$$\sigma(\epsilon_i,\theta,\epsilon_f) = \left(\frac{\beta\epsilon_f}{4\pi\epsilon_R\epsilon_i}\right)^{1/2} \sum_{\alpha\alpha'} \left(A_{l\alpha}A_{l\alpha'} + C_{l\alpha}C_{l\alpha'}\delta_{\alpha\alpha'}\right)$$

$$(\times)\; e^{-\frac{\hbar K_1^2}{4\mu\omega}(h_\alpha^2+h_{\alpha'}^2)} \sum_l (2l+1)\, j_l(K_1 b_\alpha)\, j_l(K_1 b_{\alpha'})\,(2\delta_{\alpha\alpha'}-1)^l \left\{ e^{-\frac{\beta}{4\epsilon_R}(\epsilon+\epsilon_R)^2} \right.$$

$$\left. + \frac{l(l+1)(1+e^{-\nu})}{2\eta(1-e^{-2\nu})}\left[e^{-\nu}\, e^{-\frac{\beta}{4\epsilon_R}(\epsilon+\epsilon_R-\sqrt{2\lambda\beta})^2} + e^{-\frac{\beta}{4\epsilon_R}(\epsilon+\epsilon_R+\sqrt{2\lambda\beta})^2} \right]\right\} , \qquad (6.10)$$

with $\epsilon_R = \frac{\hbar^2 K_1^2}{2M}$. The distribution of energy transfer is seen to be continuous. In the calculations we will also use this expression as a comparison with Eq. (6.8).

It is of some interest to note that the differential cross sections exhibited in Eqs. (6.8) and (6.10) both satisfy the detailed balance condition which can be stated as[23]

$$\sigma(\epsilon_1,\theta,\epsilon_2) = \sigma(\epsilon_2,\theta,\epsilon_1)\left(\frac{\epsilon_1}{\epsilon_2}\right) e^{\beta(\epsilon_2-\epsilon_1)} \quad .$$

This property of the cross section is useful in neutron thermalization studies.

THE MEASURED DIFFERENTIAL CROSS SECTION

The measured differential cross section $\bar{\sigma}(\epsilon_{io},\theta,\epsilon_{fo})$ is actually an appropriate average of $\sigma(\epsilon_i,\theta,\epsilon_f)$ since due to the inherent finite resolution associated with any energy-measuring device the initial and final neutron energies cannot be specified precisely. If we let $A(\epsilon_i,\epsilon_{io})$ and $B(\epsilon_f,\epsilon_{fo})$ be the energy distributions of the incident neutrons and the neutrons actually detected respectively, then

$$\bar{\sigma}(\epsilon_{io},\theta,\epsilon_{fo}) = \int B(\epsilon_f,\epsilon_{fo})\,d\epsilon_f \int A(\epsilon_i,\epsilon_{io})\,\sigma(\epsilon_i,\theta,\epsilon_f)\,d\epsilon_i \quad . \tag{6.11}$$

We shall approximate the incident spectrum by a Gaussian,

$$A(\epsilon_i,\epsilon_{io}) = N\, e^{-4\gamma^{-2}(\epsilon_i-\epsilon_{io})^2 \ln 2} \quad , \tag{6.12}$$

where γ is the full width at half maximum and N is the normalization constant. The distribution B will be approximated by a step function so that $B(\epsilon_f,\epsilon_{fo}) = 1$ for $\epsilon_{fo} - \frac{\Delta\epsilon}{2} \leq \epsilon_f \leq \epsilon_{fo} + \frac{\Delta\epsilon}{2}$ and zero otherwise. Then we may write

$$\bar{\sigma}(\epsilon_{i0},\theta,\epsilon_{fc}) = N\Delta\epsilon \int \sigma(\epsilon_i,\theta,\epsilon_f)\, e^{-4y^{-2}(\epsilon_i-\epsilon_{i0})^2 \ln 2}\, d\epsilon_i \, . \qquad (6.13)$$

For the following calculations we will use a scattering angle of 90° in order to obtain maximum energy transfer and a value of 0.065 ev for ϵ_{i0}. In applying Eq. (6.8) the final energy space is divided into equal intervals of $\Delta\epsilon$, then all contributions to an interval are summed and assigned a value at the midpoint of the interval. The energy distribution thus appears in the form of a histogram. The energy distribution computed with Eq. (6.10) is necessarily a smooth function so the results are presented as a curve drawn through the discrete points of computation. To compare the results obtained with Eqs. (6.8) and (6.10) the distributions are normalized at the energy in the vicinity of the incident spectrum where the scattering intensity according to (6.8) is a maximum.

SLOW-NEUTRON SCATTERING BY HYDROGEN CHLORIDE

Among the hydrogen halides, HF, HCl, HBr and HI are in the order of increasing mass and decreasing permanent electric dipole moment. From the standpoint of obtaining maximum energy transfer and applying the strong field description of hindered rotations HF should be the most appropriate scattering system. But because of the practical problem of finding suitable substance to contain HF and of the availability of optical and thermodynamic studies of HCl in the literature we have chosen HCl to perform sample calculations.

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. In the absence of Stockmayer potential parameters for HCl the method developed in Chapter III is not applicable; we shall therefore follow an approach previously employed by Morales.[15] On the basis of an oscillator description of the liquid an approximate expression has been derived relating the entropy of melting S to the ratio of oscillation frequencies in the solid and liquid states,[49,50]

$$\frac{S}{kT_m} = 3 \ln\left(\frac{3k\theta_D}{4\hbar\omega}\right) + 1 \,, \tag{6.14}$$

where T_m denotes the melting temperature. In this expression we have replaced the frequency of oscillation in the solid phase by an average frequency corresponding to a Debye temperature θ_D. Using the values[51] $T_m = 162°K$, $S = 476$ cal/mol and $\theta_D = 128°K$ we obtain $\omega = 1.112 \times 10^{13}$ sec^{-1}. This is the value of ω used in (6.8) to compute the energy distribution for HCl.

The local electric field produced by the neighboring molecules, in principle, can be estimated from the known crystalline structure. On the other hand, in infrared studies of crystalline HCl Hornig and Osberg[52] observed a line corresponding to an energy of about 0.033 ev interpreted to be a torsional lattice vibration.* We will interpret this energy to cor-

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*A weaker and broader band corresponding to 466 cm^{-1} ($\sim$ 0.0575 ev) has also been observed.

respond to the energy of hindered rotation, $\sqrt{2\lambda B}$. From the H-Cl separation of 1.2747Å [53] we find $b_H = 1.2395$Å, $b_{Cl} = 0.0352$Å, and the rotational constant B = 0.00131 ev. The dipole moment of HCl in liquid phase (162-188°K) is about 1.15 debye[54] (1 debye = 10^{18} esu), a slight increase over the gas-phase value of 1.03.[55] In order that $\sqrt{2\lambda B} \sim 0.033$ ev a field strength of about 5.77×10^5 dyne/cm will be used. This value is not unreasonable since in water the estimated field is of the same order of magnitude.

The frequency of internuclear vibration in the ground state of HCl has been reported at 5.63×10^{14} sec^{-1}.[53] This frequency corresponds to an energy of 0.35 ev so that at 188°K the population of the excited levels should be negligible. For 0.065 ev neutrons the assumption of no energy transfer with the vibrational mode is also justified. Thus our approximation of the vibrational thermal average is not expected to introduce any appreciable error.

The appropriate nuclear scattering amplitudes of hydrogen and chlorine have been measured[56] at $4\pi D_H^2 = 81\,2$, $4\pi A_H^2 = 2.01$, $4\pi D_{Cl}^2 = 15$, and $4\pi A_{Cl}^2 = 12$ in units of barn (1 barn = 10^{-24} cm^2). The scattering by hydrogen is seen to be predominantly incoherent, while the scattering by chlorine is mostly coherent.

The energy distributions of neutrons scattered by HCl at 188°K as predicted by the hindered and free translation descriptions are shown in Fig. 5. Since it is anticipated that such an experiment may be carried out here at The University of Michigan the incident spectrum used is a

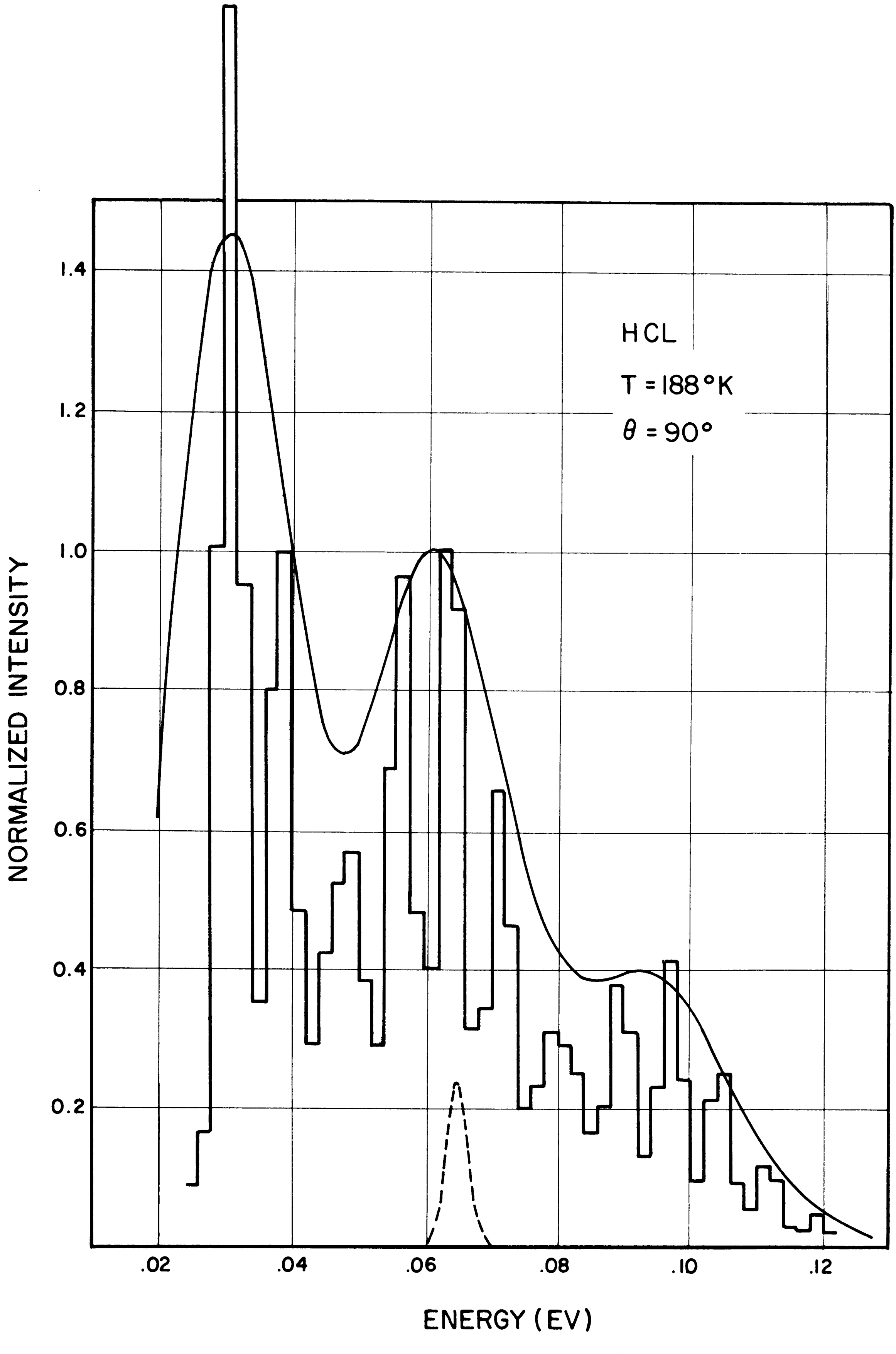

Fig. 5. Energy distributions normalized at 0.062 ev of an initially "narrow" beam of neutrons scattered by hydrogen chloride according to descriptions of hindered (histogram) and free (solid curve) translations. Also shown is the incident spectrum.

narrow Gaussian as indicated by the dotted curve where $\gamma \sim 0.05\epsilon_{io}$. This spectrum represents the optimum that can be achieved with the crystal spectrometer in the Phoenix Memorial Laboratory.[57] The result obtained according to Eq. (6.8) is presented in the form of a histogram at a uniform width of 0.002 ev, a value of $\Delta\epsilon$ that may be somewhat optimistic even for high-resolution measurements. The incident spectrum is sufficiently narrow so the hindered translation result shows considerable structure. Both distributions indicate that the two peaks associated with hindered rotation scattering should be easily measurable; consequently, an experiment measuring the intensity of scattering in these vicinities is strongly suggested as a test of the proposed model.

An identical calculation using a broad ($\gamma \sim 0.15\epsilon_{io}$) Gaussian incident spectrum shows little or no evidence of the structure due to hindered translational motions, a result not at all surprising since there now exists considerable overlap of contributions from the various direct scattering terms in (6.8). The contribution from "inner" scattering is found to be less than 1% and hence is ignored.

SLOW-NEUTRON SCATTERING BY WATER

In calculating the differential cross section for water we introduce an approximation in which the asymmetric water molecule is replaced by a fictitious diatomic molecule of equivalent mass and electric dipole moment (μ = 1.8 debye[55]). This approximation greatly simplifies the calculation of rotational thermal average and does not alter any essential feature of hindered rotations. Although the appropriate moment of inertia to be used in computing the rotational constant is now somewhat ambiguous, B can be expected to be of the order of 10^{-3} ev. The internuclear vibrational frequency of this diatomic molecule is taken to correspond to the first measured vibrational level, $\Omega = 3.12 \times 10^{14}$ sec^{-1}.[58] Using an O-H distance of 0.96Å and H-O-H angle of 105°[59] we have estimated b_H to be 0.905Å.

In obtaining the oscillation frequency ω, the Stockmayer potential for water[33] gives a value for $\gamma \sim 0.023$, thereby indicating that the potential $V(u)$ is not parabolic. Nevertheless we shall proceed to approximate the actual $V(u)$ by a parabola. If we apply Eq. (6.14) using $\theta_D \sim 250°K$[60] and $S \sim 1400$ cal/mol[61] then $\omega \sim 1.5 \times 10^{13}$ sec^{-1}. According to recent calculations of Singwi and Sjölander[18] and high-resolution neutron experiments[13] the Debye temperature for water, assuming such a concept is meaningful, is about 135°K. The frequency appropriate to the present hindered translation description is then three fourth of the frequency corresponding to this value of θ_D, or $\omega \sim 1.3 \times 10^{13}$ sec^{-1}. We shall use this latter value of ω in the calculations.

An attempt is made to estimate the magnitude of the local electric field by directly computing the field produced at the central molecule which is surrounded by four dipoles at the corners of a tetrahedron. The orientations of the dipoles are chosen to the extent that there is a hydrogen between two oxygens, otherwise they are arbitrary. The value of E computed in this manner is about 3 x 10^5 dyne/cm, thus giving λ as $\sim$ 0.35 ev which may be compared to the height of a hindering potential of $\sim$ 0.7 ev from an early calculation by Magat.[22] Since the rotational constant B is not known in the diatomic approximation we shall choose B such that $\sqrt{2\lambda\mathcal{B}}$ corresponds roughly to the observed energy of hindered rotation $\sim$ 0.06 ev,[12,13,19] then $\mathcal{B} \sim 5.3 \times 10^{-3}$ ev.

We have mentioned that scattering by hydrogen is mainly incoherent. The scattering by oxygen however is entirely coherent,[56] $4\pi D_O^2 = 4\pi A_O^2 = 4.2$ barns. On the basis of the scattering amplitudes, hydrogen effects constitute about 95% of total scattering so we will ignore the small contribution from oxygen in the following calculations.

In order to determine the nature of translational motions in water we compute the energy distributions according to the oscillator and free gas descriptions of the center-of-mass degrees of freedom and neglect, for the moment, the effects of internal degrees of freedom. The two distributions are compared in Fig. 6 where the experimental points of Brockhouse[14] are also shown. The dotted curve represents a relatively broad incident spectrum ($y \sim 0.15\epsilon_{io}$) corresponding to the actual spectrum employed in the experiment. We observe that the two descriptions give essentially the same distribution. The discrete structure associated with the hindered motions is almost completely smeared into a smooth distribution by virtue of the relatively large spread of the incident spectrum which causes considerable overlap of different transitions. On the basis of this comparison we can conclude that measure-

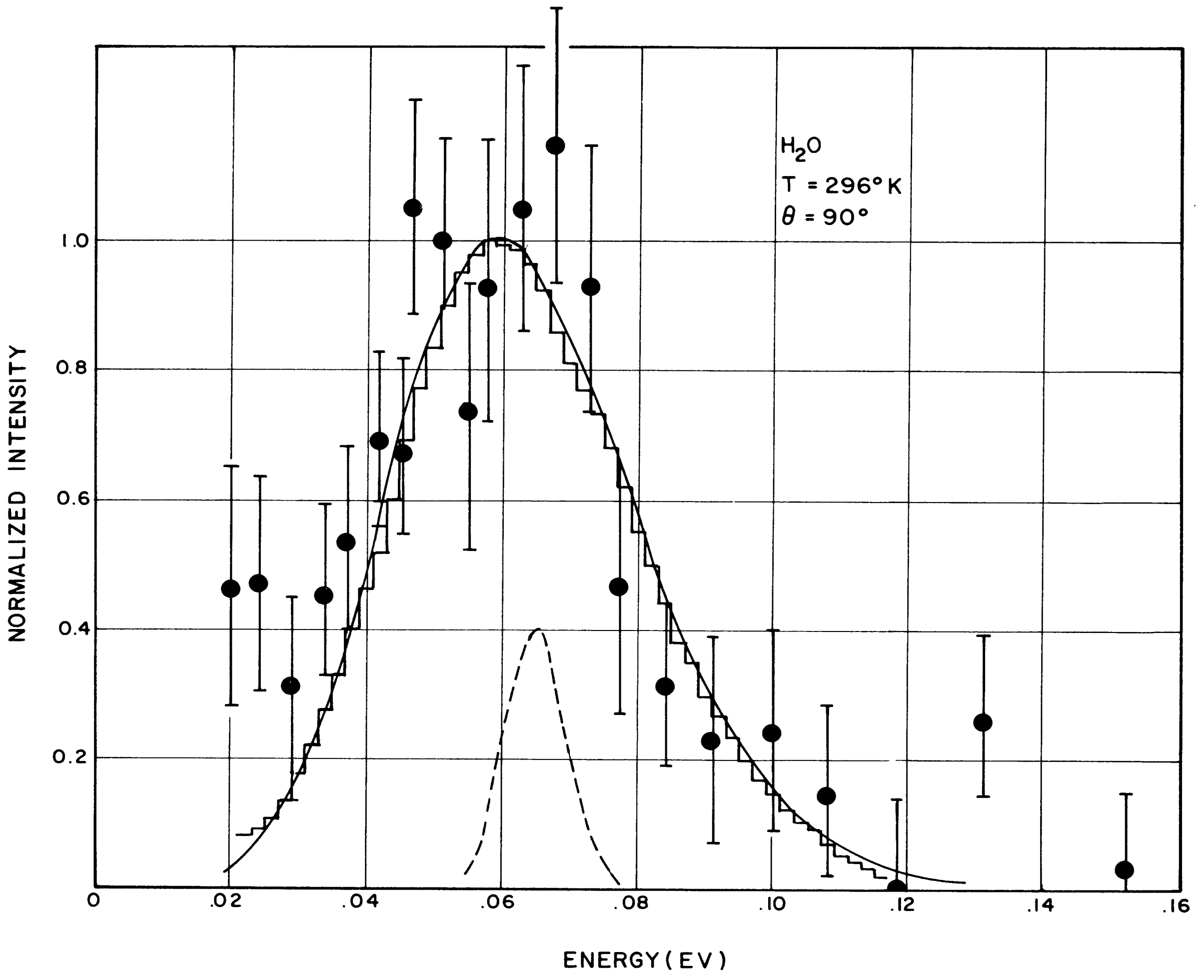

Fig. 6. Energy distributions normalized at 0.058 ev of an initially "broad" beam of neutrons scattered by water (center-of-mass degrees of freedom only) according to descriptions of hindered (histogram) and free (solid curve) translations. Also shown are the experimental points[14] normalized at 0.052 ev and the incident spectrum.

ments with the present spectrum are not sensitive to details of molecular translations and therefore cannot yield any information regarding any possible hindrances which may exist in water. This observation also explains why gas-like descriptions have been used with success in computing neutron distributions in reactors. The peaks of the two distributions in Fig. 6 are seen to be shifted to a lower energy. The observation that the broadening predicted by the hindered translation model is slightly smaller can be explained by the fact that a hindered molecule develops a thermal cloud of smaller extent during the scattering process than the free molecule. Except for the regions of large energy transfer both models give reasonable fit to the data thus indicating that the differential cross section for small energy transfer is influenced mainly by interactions with the molecule as a point mass. A similar comparison is given in Fig. 7 in which the narrow incident spectrum of Fig. 5 is used. In this case the discrete structure associated with the oscillator model is clearly observable. There is essentially no shift of the elastic peak in the hindered translation distribution where the intensity of low order (n) inelastic scattering is greater when neutron loses energy than when energy is gained. The attenuation of the higher order processes is not the same for energy gain and loss, hence the distribution becomes asymmetrical as is apparent in Fig. 6. It is noted in Fig. 7 that transitions for which $n > 5$ need not be considered since their intensities are of the order 1% or less compared to the intensity of elastic scattering.

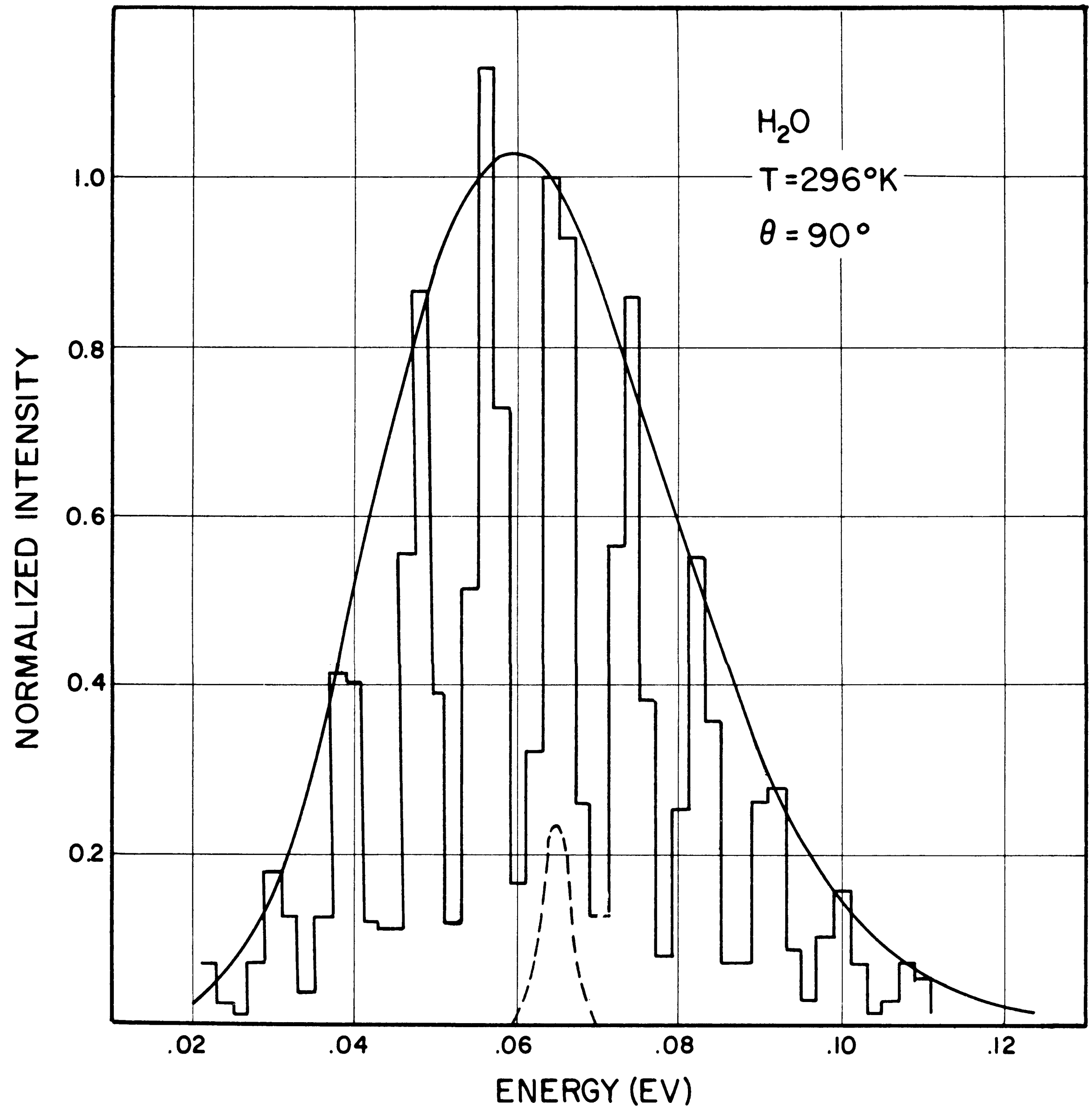

Fig. 7. Energy distributions normalized at 0.064 ev of an initially "narrow" beam of neutrons scattered by water (center-of-mass degrees of freedom only) according to descriptions of hindered (histogram) and free (solid curve) translations. Also shown is the incident spectrum.

The energy distributions for water calculated according to Eqs. (6.8) and (6.10) are shown in Fig. 8 along with the measurements of Brockhouse and the theoretical curve (dotted line) of Nelkin. The effects of zero point vibration and hindered rotation are readily observed by comparing these results with those in Fig. 6. As can be expected with a broad incident spectrum little difference exists between free and hindered translation descriptions. A value of $E = 4 \times 10^5$ dyne/cm is used in the computation which corresponds to $\sqrt{2\lambda B} = 0.069$ ev. It is observed that within the large experimental uncertainties the theoretical curves are in reasonable agreement with the measurements. The essential difference between Nelkin's theory and the present treatment manifests mainly in the predicted intensity of scattering associated with hindered rotations, the calculation in this investigation showing a considerably more pronounced effect than Nelkin's distribution. Because of experimental uncertainties and the scarcity of data in the region around 0.12 ev it is not possible to arrive at any definite conclusion regarding relative accuracy of the two models.

In cold-neutron ($\epsilon_{io} \sim 0.005$ ev) measurements of water[12,13] the observed intensity of the hindered rotation peak is about twice that at the incident energies. The intensity calculated according to (6.8) is found to be low by a factor of ~ 10. The discrepancy may indicate that symmetry effects are important in this case, hence the breakdown of the diatomic approximation. On the basis of the comparison in Fig. 8, it

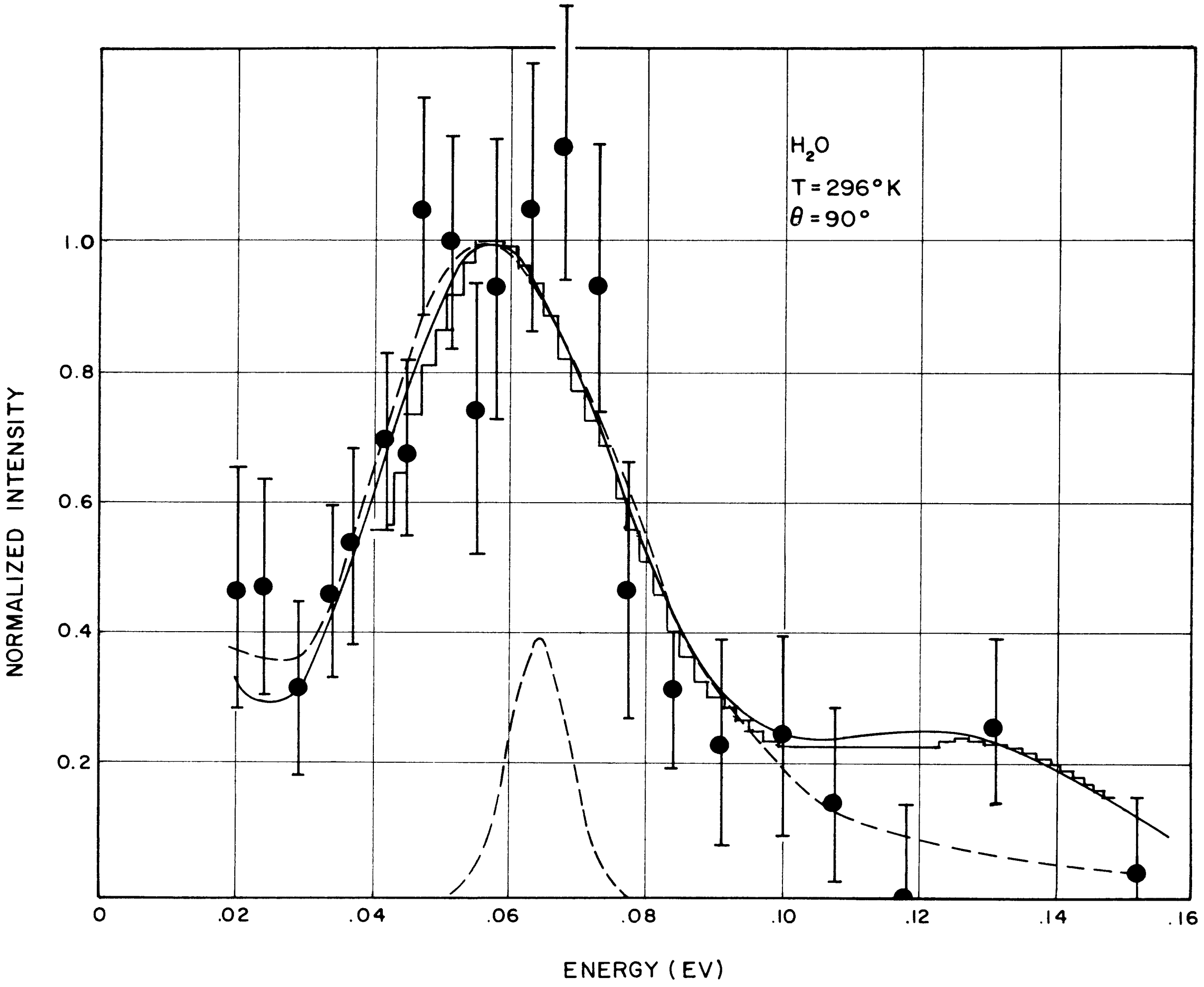

Fig. 8. Energy distributions of an initially "broad" beam of neutrons scattered by water according to descriptions of hindered (histogram) and free (solid curve) translations. Also shown are Nelkin's calculation[23] (dotted curve), the experimental points[14] normalized at 0.052 ev, and the incident spectrum. All theoretical curves are normalized at 0.058 ev.

is likely that even lower intensity will be predicted by Nelkin's model although such a calculation has not been reported. In these experiments a smaller peak corresponding to energy transfer of $\sim$0.008 ev is also observed. The position of this peak is predicted by the present model as the primary hindered translation peak although the calculated intensity is lower than the observed value by a factor $\sim$ 2.

CHAPTER VII

CONCLUDING REMARKS

By considering the effects of intermolecular forces on molecular translation and rotation the model proposed in this investigation reduces the description of slow-neutron scattering to a consideration of two parameters which characterize the scattering system, a frequency of oscillation of the center of mass and a local electric field which hinders rotation. The oscillation frequency arises from a parabolic approximation to an effective potential derived on the basis of assigning the neighboring molecules to a spherical distribution and choosing an appropriate two-particle interaction. Such a potential will always tend to confine the central molecule to one, or at most two, small local regions. The validity of the parabolic approximation then depends on the fact that the localized region of minimum interaction be necessarily at the center of the distribution. This sufficient condition can be stated essentially in terms of the ratio of the distance of closest approach, a parameter appropriate to the two-particle potential, and the radius of the spherical distribution. When the ratio is of order unity repulsive forces dominate in the interaction between the central molecule and its symmetrically-located neighbors in which case a justification for the use of an oscillator description of translational motions is obtained.

The polar nature of the molecules can be taken into account in estimating this oscillation frequency. It is found that the specific effect of dipole-dipole interaction suitably averaged over orientations produces attraction among molecules, and hence leads to a more stringent condition for the oscillator approximation. There is no aposteriori reason for choosing a spherical distribution for the neighbors; in fact, the orientation-dependent dipole-dipole effects suggest that the tendency for molecules to associate is probably greater in some directions than in others. The results of smearing the neighbors according to a prolate or oblate spheroidal distribution are complicated but are simplified considerably in the case of small deformation from spherical symmetry. The oscillator frequency estimated in this manner is now directionally dependent and contains the additional parameter characterizing the deformation.

The estimation of an oscillator frequency according to the smearing procedure is a useful method provided that in the case where the sufficient condition is not satisfied a parabola can still be found by numerical means which is a reasonable fit to the calculated effective potential. This method is, nevertheless, limited since the necessary parameters of the two-particle interaction may not be known for a specific liquid. On the other hand, such a frequency may also be estimated from a simple expression which requires only a knowledge of the entropy of melting, the melting temperature, and a characteristic frequency of oscillation in the corresponding solid. This somewhat less direct approach has a much wider range of applicability and is found to be satisfactory in the cases of lead and water.

A means by which the rotational motions of polar molecules are hindered is obtained by assigning the hindrance to purely electrostatic effects, specifically, the coupling between the dipole moment and a uniform and constant electric field. In principle, the magnitude of the field is expected to be roughly the same as the crystalline field in the corresponding solid. In practice, the field estimated from the structure of ice is found to be of the proper order of magnitude expected for water on the basis of measurements. The particular type of hindrance considered here affects only one angular displacement, so there will still be free rotational motions associated with the other two rotational degrees of freedom of the molecule.

The present description of hindered rotation leads to useful wave functions for symmetric and linear molecules under the condition of strong coupling. The energies associated with hindered rotation of both types of molecules are those of a two-dimensional isotropic oscillator with level spacing $\sqrt{2\lambda B}$, where λ and B are the coupling and rotational constants respectively. This fact is actually to be expected since for small angular displacements any molecule behaves like a torsional oscillator. The energies of this oscillator can then depend on system symmetries only through its level spacing, hence the definition of B . This observation implies that the hindered rotational energy spectrum of an asymmetric molecule should also consist of an equally-spaced set of levels. It then appears that in the sense of similar energy spectrum the effects of hindered rotation on neutron scattering by an asymmetric molecule may be approximated by those calculated using the wave functions of the symmetric, or even the diatomic, molecule. However, the asymmetry which is ignored in such an approximation may have significant influence on the scattering intensity in which case substantial error can be introduced in the calculated energy distribution of the scattered neutrons. The condition of strong coupling requires that the mean square of the angular displacement between the dipole moment and the field be small. For this reason, only a subset of the totality of the available eigenstates corresponds to physically meaningful solutions and, in principle, only these states are involved in the scattering process.

Using the present descriptions of molecular translation and rotation the differential cross section for slow-neutron scattering can be calculated without introducing further approximations. As a consequence of the assumption of no dynamical coupling between molecules inelastic processes are possible only by direct and "inner" scatterings. These effects therefore determine the energy distribution of the scattered neutrons. The purely elastic "outer" effect, which can be important in considerations of angular distributions, has not been dealt with to any appreciable extent in this investigation.

In the parabolic approximation the scattering by the center-of-mass degrees of freedom is described by the well-known results of neutron scattering by a system of independent oscillators. The method employed in treating the scattering by rotational degrees of freedom can be applied to both free and hindered molecules. In the former case the evaluation of the matrix elements is considerably facilitated by making use of known symmetry properties of the wave functions. The results obtained are particularly useful when the incident neutron energy is sufficiently low so that only the lowest order excitations contribute significantly to the cross section. In the case of hindered rotators consideration of the integrals involved leads to a separation of the different contributions to the scattering in powers of $\left(B/2\lambda\right)^{1/2}$. The zeroth-order terms in the cross section therefore consist of elastic processes and inelastic processes involving only changes in free-rotation energies. The first-order terms consist of transitions involving the exchange of $\sqrt{2\lambda B}$ in the presence of free rotation excitations. These latter terms can be interpreted to give rise to the hindered rotation transitions observed in neutron as well as optical measurements. Higher-order terms in the cross section correspond to excitations involving multiples of $\sqrt{2\lambda B}$ and also free-rotation energies; these are of much lower intensity and may be ignored (for water the second-order terms are of an order of magnitude lower in intensity as compared to the first-order terms).

When the small free-rotation energies are ignored the total scattering consists of only elastic and $\pm\sqrt{2\lambda B}$ inelastic contributions and the cross section can be exhibited in a particularly simple form. The fact that only a limited number of the hindered rotator eigenstates can be used does not impose any significant restriction on the calculation. This is because in averaging over initial states the summation involves terms in powers of $\ell^{-\nu}$ which is a small quantity ($\ell^{+\nu} \sim 8$ and 20 for HCl and H_2O respectively), and hence the inclusion of all powers of $\ell^{-\nu}$ introduces little error.

The expression for the cross section may be compared to Nelkin's model of hindered rotation.[23] The present treatment is seen to be less empirical in that all the rotational degrees of freedom are considered and the polar nature of the molecule is explicitly taken into account. In addition to the parameters which characterize the particular model the difference in the two descriptions manifests itself mainly in intensity factors.

It is recommended that the model proposed in this investigation be subjected to thorough experimental test. The calculations for hydrogen chloride and water both indicate that effects of hindered rotational motions can be observed by measuring the energy distribution of scattered neutrons. On the other hand, relatively high-resolution experiments are necessary in order to resolve the distribution in the region of small energy transfer for structure associated with hindered translational motions. Results of the water calculation are in good agreement with low-resolution measurements.[14] However, the experiment is not sufficiently precise as to provide a basis for quantitive comparison of Nelkin's model and the description presented here, even though the two calculations deviate significantly in the region where hindered rotation effects are prominent.

In view of the calculations a number of scattering experiments are suggested. It will be desirable to repeat Brockhouse's water experiment to examine with greater precision the region where prominent hindered rotation excitation ~ 0.06 ev is predicted. If sufficiently good resolution ($\sim 5\%$ resolution) can be obtained the region of small energy transfer should be studied to determine if any structure exists in the distribution. In this respect, it is perhaps more appropriate to use incident neutrons of lower energy than ~ 0.065 ev. Similar types of measurements are also highly recommended for hydrogen chloride. If energy exchanges ~ 0.033 ev of appreciable intensity are indeed observed then the neutron method promises to be a very powerful tool for the study of hindered rotations in polar liquids, particularly those liquids, such as hydrogen flouride, which may not be suitable for optical studies.

The present investigation provides a basis which can be modified and extended in subsequent work. The hindered rotation descriptions can be refined by introducing temporal and spatial dependences in the local electric field, the latter effect thus leading to directional correlation between molecules. Some consideration should be given to a description in which all three rotational degrees of freedom are hindered for the analysis of neutron scattering by systems, such as perhaps ammonium halides, which do not seem to exhibit any free rotations. Thus far, Nelkin's model has been used to study neutron thermalization and diffusion in water. It is suggested that some of the calculations be repeated using the results derived in this investigation. Since the quantities to be calculated are integral measurements of the differential cross section, no major deviation in the two models can be expected; nevertheless, second-order differences can prove to be very interesting and informative. Only qualitative agreement is obtained with the cold-neutron water data[12,13] where the calculated intensities in the diatomic approximation are considerably lower than the measured values. It appears that a more refined computation, where the molecular symmetries are treated more appropriately, is required to determine if the present model is adequate in obtaining quantitative agreement.

APPENDIX A

A NON-SPHERICAL LENNARD-JONES-DEVONSHIRE "SMEARING" PROCEDURE

We consider the derivation of an effective potential for molecular translational degrees of freedom in which the distribution of neighbors about the "equilibrium position" of the central molecule is assumed to be non-spherical. By taking all molecular dipoles to be along the same direction, say the z axis, the effective potential is given by (3.14),

$$V = \int d^3\underset{\sim}{\xi}\, P(\underset{\sim}{\xi})\, U(\underline{r}),$$

$$U(\underline{r}) = \frac{a}{r^{12}} - \frac{b}{r^6} + \frac{\mu}{r^3} - \frac{3(\underline{\mu}\cdot\underline{r})^2}{r^5}, \tag{A.1}$$

with $a = 4\epsilon\sigma^{12}$, $b = 4\epsilon\sigma^6$. The surface of distribution will be taken to be a spheroid for which we introduce ellipsoidal coordinates,[51]

$$x = \gamma_0 \sinh\alpha \sin\theta \cos\varphi,$$
$$y = \gamma_0 \sinh\alpha \sin\theta \sin\varphi,$$
$$z = \gamma_0 \cosh\alpha \cos\theta.$$

The probability of finding a molecule on a given surface ($\alpha = \alpha_0$, a constant) becomes

$$P(\underset{\sim}{\xi})\, d^3\underset{\sim}{\xi} = \left[2\pi\left(2\sinh^2\alpha_0 + \frac{4}{3}\right)\right]^{-1} \delta(\alpha-\alpha_0)(\sinh^2\alpha_0 + \sin^2\theta)\sin\theta\, d\theta\, d\alpha\, d\varphi. \tag{A.2}$$

In the present approach, a direction, that of the dipoles, has been defined for the problem, therefore it is convenient to exhibit V in terms of its components, V_z and V_{xy}, corresponding to the cases in which displacements of the central molecule are parallel and perpendicular to the dipole orientation respectively. We find

$$V_z = (2m+\tfrac{4}{3})^{-1} \int_{-1}^{1} dx\,(m+1-x^2) \left\{ \frac{a}{r^{12}} - \frac{b}{r^6} - \frac{2\mu^2}{r^3} \right\} ,$$

$$V_{xy} = (2m+\tfrac{4}{3})^{-1} \int_{-1}^{1} dx\,(m+1-x^2) \left\{ \frac{a}{r_0^{12}} - \frac{b}{r_0^6} + \frac{\mu^2}{r_0^3} \right\} , \qquad \text{(A.3)}$$

where

$$r = \left[\xi^2 + u^2 - 2\xi u x\right]^{1/2} ,$$

$$r_0 = \left[\xi^2 + u^2 + 2\xi u (1-x^2)^{1/2}\right]^{1/2} ,$$

$$\xi = \gamma\left[m + (n-m)x^2\right]^{1/2} ,$$

$$m = \sinh^2 \alpha_0 ,$$

$$n = \cosh^2 \alpha_0 .$$

Instead of performing the indicated integrations we consider the following approximation. For small displacements,

$$V \cong \int d^3\xi\, P(\xi) \left\{ U(\xi) + \left(\frac{\partial U}{\partial u_j}\right)_0 u_j + \frac{1}{2}\left(\frac{\partial^2 U}{\partial u_i \partial u_j}\right)_0 u_i u_j \right\} , \qquad \text{(A.4)}$$

where indices i,j represent different components of the vector and repeated indices are to be summed. After some manipulation it can be shown that

$$\int d^3\xi\, P(\xi) \left(\frac{\partial U}{\partial u_j}\right)_0 = 0 , \quad \text{for all } j$$

and

$$\int d^3\xi\, P(\xi)\left(\frac{\partial^2 U}{\partial u_i \partial u_j}\right)_0 = \delta_{ij}\left(A\delta_{j12} + B\delta_{j3}\right). \tag{A.5}$$

In this notation δ_{j12} denotes the x or y component and δ_{j3} the z component only; moreover $\delta_{ij}\delta_{j12}$ does not imply summation over j . We note that if $A, B > 0$ then V may be approximated by an oscillator potential with frequency in the x and y directions different from that in the z direction. Explicit expressions for (A.5) have been obtained after a great deal of manipulations. We shall merely record the results here.

$$\int d^3\xi\, P(\xi)\left(\frac{\partial^2 U}{\partial u_i \partial u_j}\right)_0 = \delta_{ij}\left\{\langle U\rangle_{LJ} + \mu^2\langle U\rangle_d\right\}, \tag{A.6}$$

where we have separated the contributions from the Lennard-Jones 6-12 potential and those from dipole-dipole interactions.

$$\begin{aligned}\langle U\rangle_{LJ} = \left[2\pi\left(2m+\tfrac{4}{3}\right)\right]^{-1}\Big\{ & 2\pi\left[\frac{6(m+1)}{\gamma_0}\left(b\Omega_4 - \frac{2a}{\gamma_0^6}\Omega_7\right) + \frac{b\Gamma_3}{\gamma_0^8(n-m)} - \frac{a\Gamma_6}{\gamma_0^{14}(n-m)}\right] \\ & + \delta_{j12}\, g_1(m+1)\left[\frac{168a}{\gamma_0^{16}}\Omega_8 - \frac{48b}{\gamma_0^{10}}\Omega_5\right] \\ & + \left[\delta_{j12}\, g_1(m+2) - \delta_{j3}\, g_2(m+1)\right]\left[\frac{12a}{\gamma_0^{16}(n-m)}\Gamma_7 - \frac{6b}{\gamma_0^{10}(n-m)}\Gamma_4\right] \\ & + \left(\delta_{j12}\, g_1 - \delta_{j3}\, g_2\right)\left[\frac{2a}{\gamma_0^{16}(n-m)^2}\left(6m\Gamma_7 - 7\Gamma_6\right) - \frac{2b}{\gamma_0^{10}(n-m)^2}\left(3m\Gamma_4 - 4\Gamma_3\right)\right]\Big\}; \end{aligned} \tag{A.7}$$

$$\langle U \rangle_d = 3\left[2\pi\left(2m+\frac{4}{3}\right)\right]^{-1}\Bigg\{-\frac{2\pi}{\gamma_c^5}\left[(n+1)\Omega^*_{5/2} + \frac{\Gamma_{3/2}}{3(n-m)}\right]$$

$$+\,\delta_{j2}\, g_1 \gamma_0^{-7}\left[(m+1)\Omega^*_{7/2} + \frac{(m+2)}{5(n-m)}\Gamma^*_{5/2} + (n-m)^{-2}\left(\frac{m}{5}\Gamma^*_{5/2} - \frac{1}{3}\Gamma_{3/2}\right)\right]$$

$$-\,\delta_{j3}\, g_2 \gamma_0^{-7}\left[\frac{(m+1)}{5(n-m)}\Gamma^*_{5/2} + (n-m)^{-2}\left(\frac{m}{5}\Gamma^*_{5/2} - \frac{1}{3}\Gamma_{3/2}\right)\right]\Bigg\}$$

$$+\,\delta_{j2}\,\frac{15 n g_1}{2\pi\gamma_c^7\left(2m+\frac{4}{3}\right)(n-m)^3}\left\{\left[n^2+nm(n-m)\right]\Gamma^*_{7/2} + \frac{7}{5}\left[2n+m(n-m)\right]\Gamma^*_{5/2} - \frac{7}{3}\Gamma_{3/2}\right\}$$

(A.8)

$$+\,\delta_{j3}\,\frac{3}{14\pi\gamma_c^7\left(2m+\frac{4}{3}\right)(n-m)^3}\Bigg\{105\gamma_c^4(m+1)(n-m)^3 g_2\,\Omega^*_{5/2}$$

$$+\left[35\gamma_c^2 g_2 (n-m)^2 - \frac{28\pi}{3}(n-m)^2 - 35 n g_2\right]\Gamma_{3/2}$$

$$+\left[\left(\frac{28\pi}{5} + 21 n g_2\right)\left\{m(n-m)+n\right\} + 21\, mn\, g_2\right]\Gamma^*_{5/2}$$

$$-\,15 nm\, g_2\left[m^2(n-1)+n\right]\Gamma^*_{7/2}\Bigg\},$$

where

$$g_1 = m\pi \gamma_0^2, \quad g_2 = 2\pi n \gamma_0^2,$$

$$\Omega_k = \frac{2(2k)!}{(2k-1)(k-1)!\,k!} \sum_{l=0}^{k-2} \frac{(k-l-1)!\,(k-l-2)!}{2^{l+1}(2m)^{l+1} n^{k-(l+1)} (2k-2l-2)!} + \frac{\tan^{-1}\sqrt{\frac{n-m}{m}}}{(2m)^{k-1}(2k-1)2^{k-2}\left[(k-1)!\right]^2 \sqrt{m(n-m)}},$$

$$\Omega^*_s = \sum_{l=0}^{s-5/2} \frac{2}{(2m)^{l+1}(2s-1)n^{s-(l+1)}} \prod_{t=0}^{l} \frac{2(s-t)-1}{s-(t+1)} + \frac{2}{(2m)^{s-3/2}(2s-1)m\sqrt{n}} \prod_{t=0}^{s-5/2} \frac{2(s-t)-1}{s-(t+1)}; \; s \geqslant \frac{5}{2}$$

$$\Omega_{3/2} = -\frac{2}{(n-m)\sqrt{n}} + (n-m)^{-3/2} \log \frac{1+\sqrt{\frac{n}{n-m}}}{\sqrt{\frac{n}{n-m}}-1},$$

$$\Gamma_k = \frac{2}{n^k} - \Omega_k,$$

$$\Gamma^*_s = \frac{2}{n^s} - \Omega^*_s.$$

These results are too complicated to be used in practice; however, in the case of small deformation from spherical smearing, $\frac{n-m}{m} \ll 1$, considerable simplifications are obtained. Using the parameters for the Stockmayer potential given by Hirschfelder[33] it has been found that for water coefficients A and B in (A.5) will be positive if $\epsilon = \frac{n-m}{m} \gtrsim 0.03$ and the elongation is in the z direction (prolate spheroid). On the other hand, if the elongation is in the x and y directions (oblate spheroid) then the coefficients are always negative, becoming more so for larger ϵ. The second case is believed to be more reasonable since for the present choice of dipole orientations the interaction is more attractive along the z direction than the x and y directions. According to the approach described in Chapter III the effective potential for water does not have a minimum around the origin since $\gamma = \frac{2}{5}\left(\frac{\sigma_0}{s}\right)^6 \simeq 0.023$ (see Figure 3).

APPENDIX B

"CREATION" AND "ANNIHILATION" OPERATORS

In Chapter III the time-dependent position operator, $\underline{u}(t) = e^{itH}\,\underline{u}\,e^{-itH}$, was introduced in (3.16). When the Hamiltonian H is that of a system of independent oscillators it is most convenient to express $u_i(t)$ in terms of certain operators of which the matrix elements in any eigenstate of the oscillator are trivially obtained. As defined, $\underline{u}(t)$ obviously satisfies the Heisenberg equation of motion

$$i\,\frac{d\underline{u}(t)}{dt} = \left[\underline{u}(t), H\right], \tag{B.1}$$

where the $\hbar$ is omitted because t here is actually the conventional $t/\hbar$. Since the oscillator is isotropic we need only to consider one of its cartesian components,

$$H = \frac{p^2}{2M} + \frac{k}{2}u^2 \;; \quad k = M\omega^2 \tag{B.2}$$

and we have the usual commutation rule $[u, p] = i\hbar$. According to (B.1),

$$i\,\dot{u}(t) = \left[u(t), H\right] = i\hbar\,\frac{p(t)}{M} \;; \quad i\,\dot{p}(t) = \left[p(t), H\right] = -i\hbar k\,u(t) .$$

These results combine to give an equation for $u(t)$, namely, $\ddot{u}(t) = -\hbar^2\omega^2 u(t)$. Thus

$$u(t) = \alpha e^{i\hbar\omega t} + \beta e^{-i\hbar\omega t} \;; \quad p(t) = iM\omega\left(\alpha e^{i\hbar\omega t} - \beta e^{-i\hbar\omega t}\right). \tag{B.3}$$

Constants α and β can be determined from $u(0)$ and $p(0)$; we find, for instance, $$u(t) = u(0)\cos\hbar\omega t + \frac{p(0)}{M\omega}\sin\hbar\omega t\,, \qquad (B.4)$$

which is in fact the result one would obtain for a classical harmonic oscillator.

An alternative approach is to consider the transformation directly,

$$u(t) = e^{itH}\,u\,e^{-itH} = u + it[H,u] + \tfrac{1}{2}(it)^2[H,[H,u]] + \cdots \qquad (B.5)$$

where $$[H,u] = -\frac{i\hbar p}{M}\,;\quad [H,u]_2 \equiv [H,[H,u]] = \frac{\hbar^2 k}{M}u$$

$$[H,u]_3 = -\frac{i\hbar^3 k}{M^2}p\,;\quad [H,u]_4 = \hbar^4\left(\frac{k}{M}\right)^2 u$$

and we have used $u(0)$, $p(0)$ interchangeably with u, p. Using these commutator results (B.5) can be summed explicitly again giving (B.4). From (B.3) we have expressions for α and β which in terms of the commutation relation for u and p satisfy $[\alpha,\beta] = -\hbar/2M\omega$; moreover, since u and p are Hermitian $\alpha^\dagger = \beta$.

It is convenient to replace the dynamical variables u and p by so-called "creation" and "annihilation" operators

$$a^\dagger(t) = \sqrt{\frac{2M\omega}{\hbar}}\,\alpha\, e^{i\hbar\omega t}\,,$$

$$a(t) = \sqrt{\frac{2M\omega}{\hbar}}\,\alpha^\dagger\, e^{-i\hbar\omega t}\,, \qquad (B.6)$$

which also have time-independent counterparts when $t = 0$. This choice produces the commutation relation $[a(t), a^\dagger(t)] = [a(0), a^\dagger(0)] = 1$.

In terms of these operators,

$$u(t) = \sqrt{\frac{\hbar}{2M\omega}}\left[a(t) + a^\dagger(t)\right] , \tag{B.7}$$

and similarly for $u(0)$. The effect of the operation of a or $a^\dagger$ on an oscillator eigenstate $|n\rangle$ can be found by the following. The Hamiltonian becomes

$$H' = (\hbar\omega)^{-1} H = \tfrac{1}{2}\left[a(t)a^\dagger(t) + a^\dagger(t)a(t)\right] = a^\dagger(t)a(t) + \tfrac{1}{2} , \tag{B.8}$$

which is also valid at $t=0$ since H itself is time-independent. We can write (B.8) as

$$(H' - \tfrac{1}{2}) = a^\dagger(0)a(0) \; ; \quad (H' + \tfrac{1}{2}) = a(0)a^\dagger(0) ,$$

$$(H' - \tfrac{1}{2})a^\dagger(0)|n\rangle = a^\dagger(0)(H' + \tfrac{1}{2})|n\rangle ,$$

or

$$H' a^\dagger(0)|n\rangle = (n+1)\, a^\dagger(0)|n\rangle ,$$

which shows that $a^\dagger(0)|n\rangle$ must be proportional to $|n+1\rangle$, i.e., $a^\dagger(0)|n\rangle = B|n+1\rangle$. Similarly we find $a(0)|n\rangle$ to be proportional to $|n-1\rangle$, or $a(0)|n\rangle = A|n-1\rangle$. To determine A and B, we simply consider

$$\langle n|a(0)a^\dagger(0)|n\rangle = n+1 \quad ; \quad \langle n|a^\dagger(0)a(0)|n\rangle = n .$$

Hence,

$$a(0)|n\rangle = \sqrt{n}\,|n-1\rangle \quad ; \quad a(t)|n\rangle = \sqrt{n}\, e^{-i\hbar\omega t}|n-1\rangle$$

$$a^\dagger(0)|n\rangle = \sqrt{n+1}\,|n+1\rangle \quad ; \quad a^\dagger(t)|n\rangle = \sqrt{n+1}\, e^{i\hbar\omega t}|n+1\rangle$$

This shows clearly why $a^\dagger$ and a are called "creation" and "annihilation" operators.

APPENDIX C

NEUTRON SCATTERING ACCORDING TO THE SQUARE-WELL APPROXIMATION

In this appendix we shall consider the thermal average $\langle e^{i\underline{K}\cdot\underline{u}_\ell(t)} e^{-i\underline{K}\cdot\underline{u}_{\ell'}}\rangle_T$ appropriate to molecules each moving in a three-dimensional square well. Since the well width is taken to be the same in all three directions we only need to treat one component in the calculation. The molecular problem is simply

$$\left\{ \frac{d^2}{d\xi^2} + \lambda^2 \right\} \psi(\xi) = 0 \;\; ; \;\; \xi \leqslant 2 \qquad (C.1)$$

where we have defined $\xi = \frac{u}{a}$, $2a$ being the width of the well, and $\lambda^2 = \frac{2MEa^2}{\hbar^2}$. The origin is chosen at $\xi = a$ with $\xi \geqslant 0$. By taking the barrier to be infinite at $\xi = 0, 2a$ the solutions to (C.1) are

$$\psi_n(\xi) = \frac{1}{\sqrt{a}} \sin \alpha_n \xi \;\; ; \;\; E_n = \frac{(\hbar \pi n)^2}{8Ma^2} \qquad (C.2)$$

where $\alpha_n = n\pi/2$.

The required matrix elements can be readily computed. For direct scattering,

$$\langle n | e^{iKu(t)} e^{-iKu} | n \rangle = \sum_m e^{it(E_n - E_m)} \left| \langle n | e^{iKu} | m \rangle \right|^2 \qquad (C.3)$$

where $$\langle m | e^{iKu} | n \rangle = \frac{iKa}{2} \left\{ \frac{e^{2iKa} \cos(m+n)\pi - 1}{(Ka)^2 - (m+n)^2\pi^2/4} - \frac{e^{2iKa} \cos(m-n)\pi - 1}{(Ka)^2 - (m-n)^2\pi^2/4} \right\} .$$

If we let $m = n \pm s$, s an integer, then

$$|\langle n| e^{iK_1 u} |n\pm s\rangle|^2 = (1-\cos 2K_1 a)G_\pm \quad ; \ s \text{ even}$$

$$= (1+\cos 2K_1 a)G_\pm \quad ; \ s \text{ odd} \tag{C.4}$$

with

$$G_\pm = \frac{(K_1 a)^2}{2}\left\{\frac{\left(\frac{s\pi}{2}\right)^2 - \frac{\pi^2}{4}(2n\pm s)^2}{\left[(K_1 a)^2 - \frac{\pi^2}{4}(2n\pm s)^2\right]\left[(K_1 a)^2 - \left(\frac{s\pi}{2}\right)^2\right]}\right\}^2 .$$

Hence the thermal average becomes, in the case of direct scattering,

$$\langle e^{iK_1 u_l(t)} e^{-iK_1 u_l}\rangle_T = \left(\sum_n e^{-E_n/k_0T}\right)^{-1} \sum_{n,s} e^{-\frac{i\hbar\pi^2 t}{8Ma^2}s(s\pm 2n)}$$

$$(\times)\ e^{-E_n/k_0T}\,|\langle n| e^{iK_1 u} |n\pm s\rangle|^2 . \tag{C.5}$$

For interference scattering,

$$\langle e^{iK_1 u_l(t)} e^{-iK_1 u_{l'}}\rangle_T = \left(\sum_n e^{-E_n/k_0T}\right)^{-1} \sum_n e^{-E_n/k_0T}\,|\langle n| e^{iK_1 u} |n\rangle|^2 . \tag{C.6}$$

In an actual calculation, the required thermal average is a product of three terms like (C.5) or (C.6) since we have only considered one component here.

APPENDIX D

ANGULAR MOMENTUM OPERATORS AND HAMILTONIAN FOR RIGID MOLECULES

The orientation of a body in space can be specified by the Eulerian angles $(\theta_1\theta_2\theta_3)$. By this we mean that the set of axes fixed in space and another set fixed in the body can be brought into coincidence by three successive rotations; explicitly,

$$\underline{l}_i''' = R_{ij}(\theta_1)\,\underline{l}_j ,$$

$$\underline{l}_i'' = R_{ij}(\theta_2)R_{jk}(\theta_1)\,\underline{l}_k ,$$

$$\underline{l}_i' = R_{ij}(\theta_3)R_{jk}(\theta_2)R_{kl}(\theta_1)\,\underline{l}_l \equiv R_{ij}\,\underline{l}_j ,$$

where $\underline{l}_i$ and $\underline{l}_i'$ are respectively the space and body axes. Since a rotation is an orthogonal transformation then matrix $R_{ij}(\theta_n)$ is orthogonal, i.e., $R^{-1}_{ij}(\theta_n) = R_{ji}(\theta_n)$. When the body is undergoing arbitrary rotation, rotation about any axis gives rise to an angular velocity $\dot{\theta}$ along that axis, and for infinitesimal rotation the angular momentum generated may be treated like vectors.[63] The angular velocity $\underline{\omega}$ for the arbitrary rotation can be expressed in terms of the Eulerian angles,

$$\underline{\omega} = \dot{\theta}_1\,\underline{l}_3 + \dot{\theta}_2\,\underline{l}_2''' + \dot{\theta}_3\,\underline{l}_3'' ,$$

where the three rotations are about $\underline{l}_3$, $\underline{l}_2'''$ and $\underline{l}_3''$ respectively (see Figure 4). Expressing the angular velocity either in the space system or the body system we have

$$\underline{\omega} = \dot{\theta}_1 \underline{\ell}_3 + \dot{\theta}_2 R_{2j}(\theta_1) \underline{\ell}_j + \dot{\theta}_3 R_{3j}(\theta_2) R_{jk}(\theta_1) \underline{\ell}_k \,, \tag{D.1}$$

$$\underline{\omega}' = \dot{\theta}_1 R^{-1}_{3j}(\theta_2) R^{-1}_{jk}(\theta_3) \underline{\ell}'_k + \dot{\theta}_2 R^{-1}_{2j}(\theta_3) \underline{\ell}'_j + \dot{\theta}_3 \underline{\ell}'_3 \,, \tag{D.2}$$

where these relations will be used in deriving angular momentum operators.

Consider an infinitesimal rotation of a scalar field $\psi(\theta_n)$ about the space axis $\underline{\ell}_j$ by an amount α_j ,

$$R\psi(\theta_n) = \Psi(\theta'_n) \equiv \psi(\theta_n + \Delta_n) \,, \tag{D.3}$$

the change in θ_n due to the rotation being $\Delta_n = \alpha_j \frac{\partial \theta_n}{\partial \alpha_j}$. Since Δ_n is small the expansion

$$\psi(\theta_n + \Delta_n) \cong \psi(\theta_n) + \Delta_n \frac{\partial}{\partial \theta_n} \psi(\theta_n)$$

is appropriate. Now define a generator of infinitesimal rotation about $\underline{\ell}_j$ as[48]

$$iL_j \equiv \lim_{\alpha_j \to 0} \left\{ \frac{\Psi(\theta'_n) - \psi(\theta_n)}{\alpha_j \psi(\theta_n)} \right\} = \lim_{\alpha_j \to 0} \frac{R - 1}{\alpha_j} \tag{D.4}$$

or

$$L_j \equiv -i \left(\frac{\partial \theta_n}{\partial \alpha_j} \frac{\partial}{\partial \theta_n} \right) = -i \left(\frac{\partial \dot{\theta}_n}{\partial \omega_j} \frac{\partial}{\partial \theta_n} \right).$$

In this rotation the summation over repeated indices is implied. By using ω'_j instead of ω_j (D.4) yields L'_j, a generator of infinitesimal rotation about the body axis $\underline{\ell}'_j$. The operator L_j is actually related to the angular momentum operator P_j by merely adding a factor, $P_j = \hbar L_j$.

ANGULAR MOMENTUM OPERATORS IN "SPACE" SYSTEM

We may regard (D.1) as a matrix equation $\omega_i = B_{in}\dot{\theta}_n$ from which we need to determine $\frac{\partial \dot{\theta}_n}{\partial \omega_i} = B^{-1}_{ni}$. In the present order of rotations

$$R(\theta_2)R(\theta_1) = \begin{pmatrix} C_2 & 0 & -S_2 \\ 0 & 1 & 0 \\ S_2 & 0 & C_2 \end{pmatrix} \begin{pmatrix} C_1 & S_1 & 0 \\ -S_1 & C_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} C_2C_1 & C_2S_1 & -S_2 \\ -S_1 & C_1 & 0 \\ S_2C_1 & S_2S_1 & C_2 \end{pmatrix},$$

where $C_i \equiv \cos\theta_i$, $S_i \equiv \sin\theta_i$. From (D.1) matrix B is seen to be

$$B = \begin{pmatrix} 0 & -S_1 & S_2C_1 \\ 0 & C_1 & S_2S_1 \\ 1 & 0 & C_2 \end{pmatrix}, \quad \text{and inverse*} \quad B^{-1} = \begin{pmatrix} -\frac{C_1C_2}{S_2} & -\frac{S_1C_2}{S_2} & 1 \\ -S_1 & C_1 & 0 \\ \frac{C_1}{S_2} & \frac{S_1}{S_2} & 0 \end{pmatrix}.$$

Hence the angular momentum operators in the space system are:**

$$P_i = -i\hbar\,\Omega_{in}\left(\frac{\partial}{\partial\theta_n}\right),$$

with

$$\Omega = (B^{-1})^T = \begin{pmatrix} -\frac{C_1C_2}{S_2} & -S_1 & \frac{C_1}{S_2} \\ -\frac{S_1C_2}{S_2} & C_1 & \frac{S_1}{S_2} \\ 1 & 0 & 0 \end{pmatrix}.$$

ANGULAR MOMENTUM OPERATORS IN "BODY" SYSTEM

We could follow the same procedure in obtaining expressions for P'_i.

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* $B^{-1} = B^{\dagger}/\det(B)$, where $B^{\dagger}$ is the adjoint matrix.

**This method of deriving P_i has been used by Osborn and Klema.[64]

However, once Ω is determined a more direct method is available. Note that

$$\begin{aligned} L'_j &= R_{jk} L_k \\ &= R_{jk} \Omega_{kn} \left(-i \frac{\partial}{\partial \theta_n}\right), \end{aligned}$$

where rotation matrix R is given by

$$R = R(\theta_3) R(\theta_2) R(\theta_1) = \begin{pmatrix} C_3C_2C_1 - S_3S_1 & C_3C_2S_1 + S_3S_1 & -C_3S_2 \\ -S_3C_2C_1 - C_3S_1 & -S_3C_2S_1 + C_3C_1 & S_3S_2 \\ S_2C_1 & S_2S_1 & C_2 \end{pmatrix}.$$

Thus

$$P'_j = -i\hbar \Omega'_{jn} \left(\frac{\partial}{\partial \theta_n}\right),$$

with

$$\Omega' = \begin{pmatrix} -\frac{C_3}{S_2} & S_3 & \frac{C_2C_3}{S_2} \\ \frac{S_3}{S_2} & C_3 & -\frac{C_2S_3}{S_2} \\ 0 & 0 & 1 \end{pmatrix}.$$

Summary: If we designate $\theta_1 = \psi$, $\theta_2 = \theta$, $\theta_3 = \phi$ according to Figure 4, then

$$P_x = \frac{\hbar}{i}\left\{-\frac{\cos\psi}{\sin\theta}\left(\cos\theta\frac{\partial}{\partial\psi} + \frac{\partial}{\partial\phi}\right) - \sin\psi\frac{\partial}{\partial\theta}\right\} \qquad P_x' = \frac{\hbar}{i}\left\{-\frac{\cos\phi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\phi}\right) + \sin\phi\frac{\partial}{\partial\theta}\right\}$$

$$P_y = \frac{\hbar}{i}\left\{-\frac{\sin\psi}{\sin\theta}\left(\cos\theta\frac{\partial}{\partial\psi} - \frac{\partial}{\partial\phi}\right) + \cos\psi\frac{\partial}{\partial\theta}\right\} \qquad P_y' = \frac{\hbar}{i}\left\{\frac{\sin\phi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\phi}\right) + \cos\phi\frac{\partial}{\partial\theta}\right\}$$

$$P_z = \frac{\hbar}{i}\frac{\partial}{\partial\psi} \qquad P_z' = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

The preceding formulae for P_i' are in agreement with Eq. (II.29) of Nielsen.[39] The present Eulerian angles are defined with respect to a right-hand coordinate system and the second rotation is about the $\underline{\ell}_2'''$ axis rather than the $\underline{\ell}_1'''$ axis as used by Goldstein,[63] Margenau and Murphy,[62] etc. If we follow Van Winter[40] who has adopted the convention of using the $\underline{\ell}_1'''$ axis for the second rotation, then

$$P_x' = \frac{\hbar}{i}\left\{\frac{\sin\phi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\phi}\right) + \cos\phi\frac{\partial}{\partial\theta}\right\}$$

$$P_y' = \frac{\hbar}{i}\left\{\frac{\cos\phi}{\sin\theta}\left(\frac{\partial}{\partial\psi} - \cos\theta\frac{\partial}{\partial\phi}\right) - \sin\phi\frac{\partial}{\partial\theta}\right\}$$

$$P_z' = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

which can be obtained from the previous results by letting $\phi \rightarrow \phi + \pi/2$.

THE HAMILTONIAN

The Hamiltonian is given by (4.2). By straightforward differentiation (using P_1') we obtain

$$-\frac{2}{\hbar^2}H_R = a\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\psi^2}-2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi}+\frac{\partial^2}{\partial\varphi^2}\right]\right\}+\frac{\partial^2}{\partial\varphi^2}+b\{-\}, \qquad \text{(D.5)}$$

where

$$\{-\} = \cos 2\varphi\left\{-\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\psi^2}-2\cos\theta\frac{\partial^2}{\partial\psi\partial\varphi}+\frac{\partial^2}{\partial\varphi^2}\right]\right.$$

$$\left.-\frac{\partial^2}{\partial\varphi^2}+2\cot\theta\frac{\partial}{\partial\theta}\right\}$$

$$+\sin 2\varphi\left\{-\frac{2}{\sin\theta}\left(\frac{\partial^2}{\partial\theta\partial\psi}-\cos\theta\frac{\partial^2}{\partial\theta\partial\varphi}\right)+\frac{2\cos\theta}{\sin^2\theta}\frac{\partial}{\partial\psi}-(1+2\cot^2\theta)\frac{\partial}{\partial\varphi}\right\}.$$

In the literature the sign of b often appears as minus[44] and is due to the use of ℓ_1''' axis instead of ℓ_2'''.

APPENDIX E

THE ASYMMETRIC MOLECULE IN AN ELECTRIC FIELD

We record here a procedure whereby, at least in principle, rigorous solutions or solutions to any order of accuracy to the problem of the hindered asymmetrical rotator can be obtained. The method is a straightforward generalization of the formal approach described in Chapter V, and, as before, involves considerable numerical efforts in any application.

The eigenvalue problem is

$$(H_R - \lambda D^1_{00} - E)\Psi = 0, \tag{E.1}$$

where H_R is the free-rotator Hamiltonian given by (4.1). From Chapter IV recall the solution

$$H_R|JEM\rangle = E_{JE}|JEM\rangle,$$

$$|JEM\rangle = \sum_{K=-J}^{J} \alpha_K(JE)|JKM\rangle.$$

Now we seek solutions to (E.1) of the form

$$|\xi M\rangle = \sum_{J=0}^{\infty}\sum_{E=0}^{2J} \beta_{JE}(\xi)|JEM\rangle, \tag{E.2}$$

since M remains as good quantum number, ξ is used to replace J and E. Henceforth we shall suppress index M. (E.1) then reads

$$\sum_{J'E'} \beta_{J'E'}(\xi)\left[(E_{JE} - E_\xi)\delta_{JJ'}\delta_{EE'} - \lambda U_{JJ',EE'}\right] = 0, \tag{E.3}$$

where $$U_{JJ',EE'} = \langle JE|D^1_{00}|J'E'\rangle = \sum_{KK'} \alpha_K(JE)\,\alpha_{K'}(J'E')\,\langle JK|D^1_{00}|J'K'\rangle ,$$

$$\langle JK|D^1_{00}|J'K'\rangle = \delta_{KK'} \sum_{\nu=|J-1|}^{J+1} C^{1\,J\,\nu}_{0\,-M}\, C^{1\,J\,\nu}_{0\,-K}\, \delta_{J'\nu} .$$

(E.3) becomes

$$\beta_{00}(\xi)(E_{00}-E_{\xi}) - \lambda \sum_{E'=0}^{2} \beta_{1E'}(\xi)\,\Omega(00,1E') = 0 , \qquad \text{(E.4)}$$

$$\beta_{JE}(\xi)(E_{JE}-E_{\xi}) - \lambda \sum_{\nu=|J-1|}^{J+1} \sum_{E'=0}^{2\nu} \beta_{\nu E'}(\xi)\,\Omega(JE,\nu E') = 0 ,$$

where

$$\Omega(JE,\nu E') \equiv \sum_{K=-(J,\nu)}^{(J,\nu)} \alpha_K(JE)\,\alpha_K(\nu E')\, C^{1\,J\,\nu}_{0\,-M}\, C^{1\,J\,\nu}_{0\,-K} . \qquad \text{(E.5)}$$

In (E.5) K ranges from -N to N, N being J or ν, whichever is the smaller. For instance,

$$\Omega(00,1E') = \alpha_0(00)\,\alpha_0(1E')\left[C^{1\,0\,1}_{0\,0}\right]^2 .$$

The first equation in (E.4) corresponds to J = 0 where ν has to be 1, and the second equation is for $J \geq 1$.

We can simplify the notations somewhat by introducing a single index η for J and E. The following correspondence is noted:

$$\begin{array}{llllll}
J = & 0 & 1 & 2 & \cdots & N \\
E = & 0 & 012 & 0\to 4 & \cdots & 0\to 2N \\
\eta = & 0 & 123 & 4\to 8 & \cdots & N^2 \to N(N+2)
\end{array} .$$

When J = N, the highest that η can assume is $\sum_{n=0}^{N}(2n+1) = N(N+1)$. Therefore in this group η starts at $(N-1)(N+1)+1 = N^2$ and runs through the $2N+1$ values of E up to $N(N+2)$. It is necessary to devise a scheme by which a given η, say $\eta = X$ can be related uniquely to a set of (J,E). Consider the test:

(1) If $X = N^2$, then the corresponding (J,E) is $J = N$, $E = 0$;

(2) If $X \neq N^2$, then find that N such that $N^2 < x < (N+1)^2$ and the corresponding (J,E) is $J = N$, $E = X - N^2$.

With this substitution (E.4) becomes

$$\beta_\eta(\xi)(E_\eta - E_\xi) - \lambda \sum_{\eta'=(N-1)^2}^{(N+2)^2-1} \beta_{\eta'}(\xi)\Omega(\eta,\eta') = 0 ; \qquad \text{(E.6)}$$

where it being understood that $N \leqslant \eta < (N+1)^2$. Equation (E.6) is in the same form as (5.4) so E_ξ and $\beta_\eta(\xi)$ can be formally expressed in similar continued-fraction forms as (5.10) and (5.11).

APPENDIX F

THE INTEGRAL $S_{ss'}(pjq;\mu)$

We shall evaluate the integral

$$S_{ss'}(pjq;\mu) = \int_0^\infty dx\, x^p e^{-(\mu+1)x} L_s^{p-j} L_{s'}^{p-q}$$

by using the generating function of associate Laguerre polynomial[41]

$$(1-t)^{-(a+1)} e^{-\frac{xt}{1-t}} = \sum_{n=0}^{\infty} \frac{t^n}{(n+a)!} L_n^a(x)$$

Consider

$$\Lambda = \sum_{nm} \frac{t^n r^m}{(n+p-j)!\,(m+p-q)!} S_{nm}(pjq;\mu)$$

$$= \frac{1}{(1-t)^{p-j+1}(1-r)^{p-q+1}} \int_0^\infty dx\, x^p e^{-\Omega x}, \qquad \text{(F.1)}$$

where $\Omega = \mu + 1 + \frac{t}{1-t} + \frac{r}{1-r}$. The integral in (F.1) is simply $p!(\Omega^{p+1})^{-1}$.

We next write

$$\Omega^{p+1} = \left[\frac{\mu(1-t)(1-r)+1-rt}{(1-t)(1-r)}\right]^{p+1},$$

so

$$\Lambda = p!(1-t)^j(1-r)^q\left[1-\{rt-\mu(1-t)(1-r)\}\right]^{-(p+1)}. \qquad \text{(F.2)}$$

The following expansions are useful:

$$\left[1-\{rt-\mu(1-t)(1-r)\}\right]^{-(p+1)} = \sum_\sigma^\infty (-)^\sigma \frac{(p+\sigma)!(1-t)^\sigma(1-r)^\sigma}{p!\,\sigma!}\left[\mu-\frac{rt}{(1-t)(1-r)}\right]^\sigma,$$

Thus
$$\left[\mu - \frac{rt}{(1-t)(1-r)}\right]^{\sigma} = \sum_{d}^{\sigma} (-)^{d} \frac{\sigma!\, \mu^{\sigma-d}}{(\sigma-d)!\, d!} \left[\frac{rt}{(1-t)(1-r)}\right]^{d} .$$

$$\left[1-\{rt-\mu(1-t)(1-r)\}\right]^{-(p+1)} = \sum_{\sigma}^{\infty}\sum_{d}^{\sigma} (-)^{\sigma+d} \frac{\mu^{\sigma-d}\,(p+\sigma)!}{(\sigma-d)!\, d!\, p!} (1-t)^{\sigma-d}(1-r)^{\sigma-d}(rt)^{d} .$$

Since j and q can be positive, negative or zero we need to consider three cases separately.

(1) <u>j and q either positive or zero</u>

$$(1-t)^{j+\sigma-d} = \sum_{u}^{j+\sigma-d} (-)^{u} \frac{(j+\sigma-d)!}{(j+\sigma-d-u)!\, u!} t^{u} ,$$

$$(1-r)^{q+\sigma-d} = \sum_{z}^{q+\sigma-d} (-)^{z} \frac{(q+\sigma-d)!}{(q+\sigma-d-z)!\, z!} r^{z} ,$$

$$\Lambda = \sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\sum_{u}^{j+\sigma-d}\sum_{z}^{q+\sigma-d} (-)^{\sigma+d+u+z}$$

$$(x)\ \frac{\mu^{\sigma-d}\,(p+\sigma)!\,(j+\sigma-d)!\,(q+\sigma-d)!\, t^{u+d}\, r^{z+d}}{(\sigma-d)!\, d!\, u!\, z!\,(j+\sigma-d-u)!\,(q+\sigma-d-z)!}$$

From this we want coefficient $t^{\varsigma} r^{\varsigma'}$, so we set $u+d=\varsigma$ $z+d=\varsigma'$ thus implying $j+\sigma \geq \varsigma, q+\sigma \geq \varsigma'$. Now we obtain

$$\mathcal{S}_{\rho\rho'}(p\,j\,q;\mu) = (-)^{\rho+\rho'}(\rho'+p-q)!\,(\rho+p-j)!\sum_{\sigma}^{\infty}\sum_{d}^{\sigma}\frac{(-)^{\sigma+d}\,\mu^{\sigma-d}\,(p+\sigma)!\,(j+\sigma-d)!\,(q+\sigma-d)!}{d!\,(\sigma-d)!\,(\rho'-d)!\,(\rho-d)!\,(j+\sigma-\rho)!\,(q+\sigma-\rho')!} \quad (\text{F.3})$$

with $d < \min\begin{pmatrix}\rho+1\\ \rho'+1\end{pmatrix}$ and $\sigma > \max\begin{pmatrix}\rho-j-1\\ \rho'-q-1\end{pmatrix}$.

When $\mu = 0$, only non-vanishing term is $\sigma = d$.

$$\mathcal{S}_{\rho\rho'}(p\,j\,q) = (-)^{\rho+\rho'}(\rho'+p-q)!\,(\rho+p-j)!\,q!\,j!\sum_{\sigma}\frac{(p+\sigma)!}{\sigma!\,(\rho'-\sigma)!\,(\rho-\sigma)!\,(j+\sigma-\rho)!\,(q+\sigma-\rho')!}, \quad (\text{F.4})$$

with max. $\begin{pmatrix}\rho'-q-1\\ \rho-j-1\end{pmatrix} < \sigma < \min\begin{pmatrix}\rho'+1\\ \rho+1\end{pmatrix}$.

(2) j <u>negative</u>, q <u>positive</u> <u>or</u> <u>zero</u>

In this case

$$\Lambda = \sum_{\sigma}^{\infty}\sum_{d}^{\sigma}(-)^{\sigma+d}\frac{\mu^{\sigma-d}\,(1-t)^{\sigma-d}\,(1-r)^{q+\sigma-d}\,(rt)^{d}}{(\sigma-d)!\,d!\,(1-t)^{|j|}} .$$

We can still expand

$$(1-t)^{-|j|} = \sum_{f}^{\infty}\frac{(|j|+f-1)!}{(|j|-1)!\,f!}\,t^{f} .$$

Thus

$$\mathcal{S}_{\rho\rho'}(p,-|j|\,q;\mu) = (-)^{\rho+\rho'}(\rho'+p-q)!\,(\rho+p-j)!$$

$$(\times)\sum_{\sigma}\sum_{d}^{\sigma}\sum_{f=\rho-\sigma}^{\rho-d}(-)^{f+\sigma+d}\frac{\mu^{\sigma-d}(p+\sigma)!\,(q+\sigma-d)!\,(|j|+f-1)!}{d!\,f!\,(|j|-1)!\,(\sigma+f-\rho)!\,(\rho-f-d)!\,(\rho'-\sigma)!\,(q+\sigma-\rho')!} . \quad (\text{F.5})$$

Again when $\mu=0$, $d=\sigma$ then only the term with $f=\varsigma-\sigma$ survives in the f summation. Also note symmetry in (ς, j) and (ς', q).

(3) j and q negative

Similar procedure leads to

$$S_{\varsigma\varsigma'}(p,-|j|,-|q|;\mu) = (-)^{\varsigma+\varsigma'}(\varsigma'+p-|q|)!(\varsigma+p-|j|)! \tag{F.6}$$

$$(x)\sum_{\sigma}\sum_{d}^{\sigma}\sum_{f=\varsigma-\sigma}^{\varsigma-d}\sum_{g=\varsigma'-\sigma}^{\varsigma'-d}(-)^{f+g+\sigma+d}$$

$$(x)\frac{\mu^{\sigma-d}(p+\sigma)!(\sigma-d)!(|j|+f-1)!(|q|+g-1)!}{d!f!g!(|j|-1)!(|q|-1)!(\sigma+f-\varsigma)!(\sigma+g-\varsigma')!(\varsigma-f-d)!(\varsigma'-g-d)!}.$$

When $\mu=0$ set $d=\sigma$, $f=\varsigma-\sigma$, $g=\varsigma'-\sigma$.

APPENDIX G

THE HINDERED ROTATOR—OSCILLATOR APPROXIMATION*

We shall consider an approximation in which Eq. (5.13) can be reduced to the oscillator equation. Equation (5.13) is

$$\left\{\frac{d^2}{d\theta^2}+\cot\theta\frac{d}{d\theta}-\frac{(M-K\cos\theta)^2}{\sin^2\theta}+\lambda'\cos\theta+\omega\right\}Y(\theta)=0, \qquad (5.13)$$

where $\lambda'=\frac{\lambda}{B}$, $\omega=\frac{E}{B}-\frac{I}{I_z}K^2$. The first-order derivative can be eliminated by the transformation $Q(\theta)=(\sin\theta)^{1/2}Y(\theta)$. Then

$$\left\{\frac{d^2}{d\theta^2}-V_{eff}(\theta)+\left(\omega+\frac{1}{4}\right)\right\}Q(\theta)=0, \qquad (G.1)$$

with

$$V_{eff}(\theta)=-\lambda'\cos\theta+\frac{(M-K\cos\theta)^2-1/4}{\sin^2\theta}.$$

For $\lambda'\gg 1$ and $M\neq K$, $V_{eff}(\theta)$ has a minimum at $\theta=\theta_m$ which is near $\theta=0$. We can therefore expand $V_{eff}(\theta)$ in a Taylor series,

$$V_{eff}(\theta)\cong V_{eff}(\theta_m)+\frac{1}{2}\left(\frac{d^2V_{eff}}{d\theta^2}\right)_{\theta_m}(\theta-\theta_m)^2, \qquad (G.2)$$

where by definition $\left(\frac{dV_{eff}}{d\theta}\right)_{\theta_m}\equiv 0$. It is found that for small θ_m

$$\theta_m^4\cong 2\left[(M-K)^2-1/4\right]/\lambda'+O(\theta_m^2/\lambda'),$$

So

$$V_{eff}(\theta_m)\cong-\lambda'+\sqrt{2\lambda'\left[(M-K)^2-1/4\right]}+K(M-K)+(M-K)^2/3,$$

$$\left(\frac{d^2V_{eff}}{d\theta^2}\right)_{\theta_m}\cong 4\lambda'+O(1/\theta_m^2).$$

---

*We thank Professor K. Hecht for a discussion of this approach which has recently been used by Maker.[65]

We have kept terms independent of λ' in $V_{eff}(\theta_m)$ because they represent the energies of free rotation which are of some interest. On the other hand, the leading terms which are ignored in $\left(d^2V_{eff}/d\theta^2\right)_{\theta_m}$, when multiplied by a term $\sim \theta_m^2$, are of the same order, but they are neglected becuase their presence introduce undesirable coupling effects between the different degrees of freedom characterized by ψ, θ and φ.

In the present approximation (G.1) thus becomes an oscillator equation. The energy eigenvalues are

$$E_{sKM} = -\lambda + \sqrt{2\lambda B}\left(2s + \sqrt{(M-K)^2 - \frac{1}{4}} + 1\right) + BMK$$
$$+ B\left(\frac{I}{I_z} - 1\right)K^2 + \frac{B}{3}(M-K)^2 - \frac{B}{4} . \qquad (G.3)$$

For $M \neq K$ we can ignore the 1/4 so (G.3) agrees with (5.19) to within a constant. The result (G.3) actually is not valid for M = K in which case $V_{eff}(\theta)$ has no true minimum. The reason for this behavior may be seen from the fact that $\theta = 0$ is a simple pole in the differential equation and physically the molecule can never be in the position $\theta = 0$ ($\underline{\mu}$ and $\underline{E}$ colinear) unless M = K. It is therefore not surprising that the M = K case leads to difficulty in the present approximation. If we insist on ignoring the $1/4\sin^2\theta$ term and proceed with the oscillator approximation then essentially we are neglecting effects of irregular behavior near the origin whenever M = K. For large λ' this irregularity is confined to a very small region about $\theta = 0$ hence the oscillator approach may still be useful in cases where one is primarily interested in the over-all behavior of the wave function.

The eigenfunctions of the hindered rotator are

$$|\varsigma KM\rangle = (2\pi)^{-1}\left(\frac{2}{\varsigma!\,2^{\varsigma}\sqrt{\pi}}\right)^{1/2} e^{iM\psi}\, e^{iK\phi}\, \theta^{-1/2}\, e^{-\frac{\theta}{2}}\, H_{\varsigma}(\theta) \qquad (G.4)$$

where H_{ς} is the Hermite polynomial of order ς. In this case, θ has the range $(-\infty, +\infty)$.

APPENDIX H

EFFECTS OF FREE ROTATION IN NEUTRON SCATTERING BY HINDERED ROTATORS

In this appendix we shall examine the influence of free-rotation energies upon the scattered neutron energy distribution. It has been shown in Chapter V that to order $\frac{1}{4\eta}$ in the cross section only the cases $m=k$ and $m=k\pm1$ need to be considered. For these cases the selection rules for ς' as given by $\delta_{\varsigma\varsigma'}$ show that $m=k$ corresponds to no excitation of the hindered modes, therefore when free-rotation energies are considered this particular case will give rise to energy transfer involving terms proportional to B. On the other hand, the cases $m=k\pm1$ correspond to "one-quantum" excitations, and in the presence of free-rotation excitations the amount of energy exchanged will not be precisely $\sqrt{2\lambda B}$ thus resulting in a broadening of the inelastic peaks at $\epsilon_f=\epsilon_i\pm\sqrt{2\lambda B}$. Since the two effects just mentioned arise from different relative values of m and k they can be discussed separately.

(1) SMALL ENERGY TRANSFER

In (5.42) $(2\eta F)^2$ is given as a sum of three terms, the first of which is $\delta_{mk}\,\delta^2_{\varsigma\varsigma'}(\bar{h}00)$. The contribution of this term in (5.41) will be denoted as

$$W_0(\varsigma,K,M,t)=e^{it(E_{\varsigma KM}-E_{\varsigma\,{K-k \atop M-k}})}\,, \qquad \text{(H.1)}$$

where now $E_{\varsigma KM}$ is given by (5.18),

$$E_{\varrho K M} - E_{\substack{\varrho K-k \\ M-k}} = B\left\{k(M+K-k) + \left(\frac{I}{I_z} - 1\right)k(2K-k)\right\}$$

$$= Bk\left\{(M-K) + \frac{I}{I_z}(2K-k)\right\} . \qquad \text{(H.2)}$$

Thus elastic scattering is obtained only when k = 0. It is interesting to note that in the case of linear molecules all terms vanish except those with k = 0 [see (5.50)] and so no small energy transfer is possible. The corresponding thermal average may be written as

$$\langle \alpha\alpha' \rangle_T^0 = 4\pi\gamma \sum_l j_l(\kappa b_\alpha) j_l(\kappa b_{\alpha'}) \sum_{k=-l}^{l} Y_l^{k*}(\hat{b}_\alpha) Y_l^{k}(\hat{b}_{\alpha'})$$

$$(\times) \sum_{\varrho K} \sum_{n=0}^{\infty} e^{-\beta E(\varrho K n)} e^{itBk\left[\pm n + \frac{I}{I_z}(2K-k)\right]} , \qquad \text{(H.3)}$$

with $\gamma^{-1} = \sum_{\varrho K n} e^{-\beta E(\varrho K n)}$,

$$E(\varrho K n) = \sqrt{2\lambda B}\,(\varrho + n) + BK\left(\frac{I}{I_z} \pm n\right) + \frac{Bn^2}{3} .$$

In (H.3) the summand actually consists of two terms corresponding to upper and lower signs of n, and similarly in γ^{-1}. The elastic term is still $j_0(\kappa|\underline{b}_\alpha - \underline{b}_{\alpha'}|)$.

(2) LARGE ENERGY TRANSFER

The preceding discussion shows how free rotational motions can lead to low-energy inelastic scattering. Now we shall consider the effects of free rotations on large energy transfer processes. The inelastic terms in (5.45) and (5.46) become

$$W_1(s,k=M,t) = \frac{(l-k)(l+k+1)}{4\eta}\sum_{s'}\left[(s+1)\delta_{ss'} + s\delta_{s's-1}\right]e^{itE_+(k=M)}$$

$$+ \frac{(l+k)(l-k+1)}{4\eta}\sum_{s'}\left[(s+1)\delta_{ss'} + s\delta_{s's-1}\right]e^{itE_-(k=M)} ,$$

$$W_1(s,k<M,t) = \frac{(l-k)(l+k+1)}{4\eta}\sum_{s'}\left[(s+\bar{h})\delta_{ss'} + (s+1)\delta_{s's+1}\right]e^{itE_+(k<M)}$$

$$+ \frac{(l+k)(l-k+1)}{4\eta}\sum_{s'}\left[(s+\bar{h}+1)\delta_{ss'} + s\delta_{s's-1}\right]e^{itE_-(k<M)} ,$$

$$W_1(s,k>M,t) = \frac{(l-k)(l+k+1)}{4\eta}\sum_{s'}\left[(s+\bar{h}+1)\delta_{ss'} + s\delta_{s's-1}\right]e^{itE_+(k>M)}$$

$$+ \frac{(l+k)(l-k+1)}{4\eta}\sum_{s'}\left[(s+\bar{h})\delta_{ss'} + (s+1)\delta_{s's+1}\right]e^{itE_-(k>M)} ,$$

where

$$E_{\pm}(K=M) = \sqrt{2\lambda B}\,[2(\rho-\rho')-1] + B[2kK - k^2 \pm (K-k)] + \Gamma - \frac{B}{3}$$

$$E_{\pm}(K<M) = \sqrt{2\lambda B}\,[2(\rho-\rho')\pm 1] + B[k(M+K) - k^2 \pm (K-k)] + \Gamma - \frac{B}{3}(1\mp 2\bar{h})$$

$$E_{\pm}(K>M) = \sqrt{2\lambda B}\,[2(\rho-\rho')\mp 1] + B[k(M+K) - k^2 \pm (K-k)] + \Gamma - \frac{B}{3}(1\mp 2\bar{h})$$

with $\Gamma = B(\frac{I}{I_z} - 1)k(2K-k)$. Hence

$$4\eta W_1(\rho, K=M, t) = e^{it[Bk(2K-k)+\Gamma-\frac{B}{3}]}$$
$$(\times)\left[(l-k)(l+k+1)\,e^{itB(K-k)} + (l+k)(l-k+1)\,e^{-itB(K-k)}\right]\left[\rho\, e^{it\sqrt{2\lambda B}} + (\rho+1)\,e^{-it\sqrt{2\lambda B}}\right],$$

$$4\eta\{W_1(\rho, K<M, t) + W_1(\rho, K>M, t)\} = e^{it\{Bk[(M+K)-k]+\Gamma-\frac{B}{3}\}}$$
$$(\times)\left[(2\rho+\bar{h})\,e^{it\sqrt{2\lambda B}} + (2\rho+\bar{h}+2)\,e^{-it\sqrt{2\lambda B}}\right]$$
$$(\times)\left[(l-k)(l+k+1)\,e^{itB(K-k+2\bar{h})} + (l+k)(l-k+1)\,e^{-itB(K-k+2\bar{h})}\right].$$

These results may be compared to (5.45) and (5.47). The major effects due to free-rotations appear in the time dependence of the matrix elements and greatly complicates the inelastic spectrum. Because the energy now depends separately in M and K the thermal average can no longer be given in closed form as (5.49), nevertheless, the expression can be written down without difficulty.

APPENDIX I

SEPARATION OF ROTATION AND VIBRATION IN DIATOMIC POLAR MOLECULES

The procedure for treating rotational and vibrational motions of a diatomic molecule is well known.[66] The method is equally applicable when the molecule is in a potential field. In the following we give a brief description to illustrate the necessary approximations in separating rotation and vibration.

The six coordinates of a diatomic molecule are chosen to be the coordinates of center-of-mass, the interatomic separation, and the two angles specifying the orientation of the molecular axis. The molecular energy is therefore just the sum of energies associated with center-of-mass and internal motions. Explicitly

$$H = H_T + H^I, \qquad (I.1)$$

with

$$H_T = \frac{P^2(\underline{R})}{2M} + V_T(\underline{R}) \qquad (I.2)$$

$$H^I = -\frac{\hbar^2}{2\tau}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right.$$
$$\left. + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + V(r) + V_R(\theta)\right\}, \qquad (I.3)$$

where $V_T(\underline{R})$ is the effective potential governing translations and therefore depending on the center-of-mass coordinate $\underline{R}$ only, and $V_R(\theta)$, as discussed in Chapter V, is a function only of the angle θ under appropriate choice of axes. The interatomic potential $V(r)$ governs the vibrational motion and hence depends on the interatomic separation. The reduced mass $\frac{m_1 m_2}{M}$, where $M = m_1 + m_2$, is denoted here as τ .

It is apparent from the form of (I.3) that the wave function describing the internal degrees of freedom is separable,

$$\psi_i(\underline{r}) = R(r)\Phi(\varphi)\Theta(\theta) \tag{I.4}$$

where

$$\Phi_M(\varphi) = e^{iM\varphi} \tag{I.5}$$

and R and Θ satisfy respectively,

$$\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{2\tau}{\hbar^2}\left[V(r) - E^I\right] - \frac{BE_R}{r^2}\right\}R(r) = 0 , \tag{I.6}$$

$$\left\{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{M^2}{\sin^2\theta} - \frac{V_R(\theta)}{B} - E_R\right\}\Theta(\theta) = 0 . \tag{I.7}$$

In arriving at (I.7) we have employed the approximation $r^2 V_R(\theta) \simeq r_\ell^2 V_R(\theta)$, r_ℓ being the separation when both atoms are at rest. Rotational constant is defined as before, $B \equiv \hbar^2/2\tau r_\ell^2$, and E^I represents the energies of internal motion. The rotational energy E_R of a diatomic molecule under the influence of a strong local electric field is given by Eq. (5.22) as E_{SM} and the associated wave function $\Phi(\theta)$ is given by (5.21) as $|SM\rangle$.

The potential for vibrational motion, to a fair approximation, can be given by a Hooke's-law interaction of the form $V(r) = \frac{b}{2}(r - r_\ell)^2$, where b is the restoring force constant. To take advantage of this quadratic form we introduce the transformation, $R(r) = Q(r)/r$ and $\rho = (r - r_\ell)$, so that

$$Q''(\rho) - \left[\frac{BE_R}{(r_\ell+\rho)^2} - \frac{2\tau}{\hbar^2}\left(E^I - \frac{b\rho^2}{2}\right)\right]Q(\rho) = 0 . \qquad (I.8)$$

The choice of $V(r)$ presupposes ρ to be small compared to r_ℓ. Then to order ρ^2 (I.8) becomes

$$Q'' + \left[W' + \frac{2s}{r_\ell^3}\rho - \left(\frac{\tau b}{\hbar^2} + \frac{3s}{r_\ell^4}\right)\rho^2 + \cdots\right]Q = 0 , \qquad (I.9)$$

where $W' = \frac{2\tau}{\hbar^2}E^I - \frac{s}{r_\ell^2}$, $s = BE_{SM}$. We observe that (I.9) resembles the oscillator equation if the term proportional to ρ can be eliminated. This is accomplished by letting $\rho = \xi + a$, and

$$Q''(\xi) + (W'' - t\xi^2)Q(\xi) = 0 , \qquad (I.10)$$

with $W'' = \frac{2\tau}{\hbar^2}E^I - \frac{s}{r_\ell^2} + ta^2$, $t = \frac{s}{a r_\ell^3}$, $a = \frac{r_\ell}{3}\left(1 - \frac{b r_\ell}{6\lambda}\right)^{-1}$ and $\lambda = \mu E$. It is seen that t is always negative because the ratio $b r_\ell^2/6\lambda \sim r_\ell^2/6\langle\rho^2\rangle$ is expected to be considerably greater than unity. Equation (I.10) is the oscillator equation provided we can ignore the fact that the actual problem requires $Q = 0$ for $r = 0, \infty$ whereas the oscillator solution vanishes at $\xi = -\infty, \infty$.

If the oscillator approximation is adopted E^{I} can then be exhibited as

$$E_{k\varsigma M} = \frac{\hbar^2}{2\tau} t^{1/2}(2k+1) + \frac{s}{r_e^2} + ta^2$$

$$\cong \hbar\Omega(k+\tfrac{1}{2}) + E_{\varsigma M} - \frac{1}{\tau}\left(\frac{E_{\varsigma M}}{r_e\Omega}\right)^2, \qquad \text{(I.11)}$$

where $\Omega = (b/\tau)^{1/2}$ is the vibrational frequency. The three terms in this equation obviously represent the energies of vibration, rotation, and rotation-vibration coupling. For most cases $\left(\frac{E_R}{\hbar\Omega}\right)^2 \ll 1$, and since $E_R > B$ we may ignore the stretching of the molecule due to rotation in which case vibration and rotation become separable. We thus find $H^{I} \cong H_V + H_R$ and $|k\varsigma M\rangle \cong |k\rangle\,|\varsigma M\rangle$, where $|k\rangle$ is the wave function of an oscillator of mass τ and associated frequency Ω.

APPENDIX J

THE THERMAL AVERAGE FOR INTERNAL DEGREES OF FREEDOM OF A DIATOMIC MOLECULE

We consider a formal method of evaluating the thermal average $\langle \chi^{J}_{2l\,\alpha\alpha'} \rangle_T$. The vibrational thermal average is given by Eq. (6.3). In general $\hbar\Omega > 2kT$ and $\hbar k^2/4\tau < \Omega$, the small argument expression of the modified Bessel function can therefore be used, $I_n(x) \sim (x/2)^n/n!$. We find

$$V_{\alpha\alpha'} = e^{itH_R}\, e^{-D'(h_\alpha \underline{k}\cdot\underline{\hat{b}}_\alpha)^2}\, e^{-itH_R}\, e^{-D(h_{\alpha'} \underline{k}\cdot\underline{\hat{b}}_{\alpha'})^2}$$

$$+ P'(e^{i\hbar\Omega t}\, e^{-\pi'} + e^{-i\hbar\Omega t}\, e^{\pi'})\, e^{itH_R}\, g_\alpha\, e^{-itH_R}\, g_{\alpha'} \tag{J.1}$$

$$+ \cdots,$$

where

$$D' = (\hbar \coth \pi')/4\tau\Omega,$$

$$P' = (\hbar \operatorname{csch} \pi')/4\tau\Omega,$$

$$\pi' = \hbar\Omega/2kT,$$

$$g_\alpha = (h_\alpha \underline{k}\cdot\underline{\hat{b}}_\alpha)\, e^{-D(h_\alpha \underline{k}\cdot\underline{\hat{b}}_\alpha)^2}.$$

The first two terms in $V_{\alpha\alpha'}$ correspond to elastic and first-order $(n = \pm 1)$ inelastic scatterings. Dependence upon H_R is explicit so that each term may be inserted into Eq. (6.1) to perform the average over molecular orientation.

We consider the first term of $V_{\alpha\alpha'}$ which represents the effects of zero vibration in (6.1). The corresponding thermal average

$$\langle X^{I\,0}_{\ell\ell\,\alpha\alpha'}\rangle_T = \sum_{SM} P_{SM}\langle SM|\, e^{itH_R}\, e^{i\underline{K}\cdot\underline{b}_\alpha}\, e^{-D'(h_\alpha\underline{K}\cdot\hat{\underline{b}}_\alpha)^2}$$

$$(x)\; e^{-itH_R}\, e^{-i\underline{K}\cdot\underline{b}_{\alpha'}}\, e^{-D'(h_{\alpha'}\underline{K}\cdot\hat{\underline{b}}_{\alpha'})^2}\,|SM\rangle . \tag{J.2}$$

In performing the average over all directions of the electric field the exponential $e^{i\underline{K}\cdot\underline{b}}$ can be expanded according to Eq. (5.26), similarly

$$e^{-D'(h_\alpha\underline{K}\cdot\hat{\underline{b}}_\alpha)^2} = 1 - \left(\frac{4\pi}{3}\right)^2 D'(Kh_\alpha)^2$$

$$(x)\sum_{stpq} Y_1^s(\hat{\underline{b}}_\alpha)\, Y_1^{t*}(\hat{\underline{b}}_\alpha)\, Y_1^{p*}(\hat{\underline{K}}^0)\, Y_1^q(\hat{\underline{K}}^0)\, D^1_{-p,-s}\, D^1_{-q,-t} + \cdots . \tag{J.3}$$

The leading term in (J.3) leads to the result given in Chapter V and the second term when inserted in (J.2) can be reduced using the **relations** (4.37) and the explicit form of $|SM\rangle$. After a series of manipulations we obtain to order $D'K^2$

$$\langle X^{I\,0}_{\ell\ell\,\alpha\alpha'}\rangle_T = \langle\alpha\alpha'\rangle_T - D'K^2\langle\;\rangle_T \tag{J.4}$$

where $\langle \alpha\alpha' \rangle_T$ is given by Eq. (5.50) and

$$\langle\,\rangle_T = 2(2\pi)^4 \sum_{\substack{\rho\rho' M \\ \ell\ell' m m'}} (-)^{\frac{\ell+\ell'}{2}} (2\ell+1)(2\ell'+1)\, j_\ell(K_\nu b_\alpha)\, j_\ell(K_\nu b_{\alpha''})\, P_{\rho M}$$

$$(\mathrm{x})\; N^2_{\rho M} N^2_{\rho' M+m}\, e^{it(E_{\rho M} - E_{\rho' M+m})}$$

$$(\mathrm{x}) \Big\{ h^2_\alpha (\rho' M+m | d^{\ell'}_{0,-m'} | \rho M) \sum_{\lambda\alpha\nu st} (2\lambda+1)^{-1} C^{\ell\;1\;\lambda}_{0\;0}\, C^{\ell'\;1\;\lambda}_{0\;0}\, C^{\ell\;1\;\lambda}_{-m\;-t}\, C^{\ell'\;1\;\lambda}_{-m'\;-s}$$

$$(\mathrm{x})\; (-)^{m+t}\, C^{\nu\;1\;\alpha}_{0\;0}\, C^{\ell\;1\;\nu}_{0\;0}\, C^{\nu\;\;1\;\;\alpha}_{(m+t)\;-s}\, C^{\ell\;1\;\nu}_{-m\;-t}$$

$$(\mathrm{x})\; (\rho M | d^{\alpha}_{0,(m+t)-s} | \rho' M+m)\, \delta_{m+t,\, m'+s}$$

(J.4)

$$+\; h^2_{\alpha'} (\rho M | d^{\ell}_{0,m} | \rho' M+m) \sum_{\lambda\alpha\nu s' t'} (2\lambda+1)^{-1} C^{\ell\;1\;\lambda}_{0\;0}\, C^{\ell'\;1\;\lambda}_{0\;0}\, C^{\ell\;1\;\lambda}_{-m\;-t'}\, C^{\ell'\;1\;\lambda}_{-m'\;-s'}$$

$$(\mathrm{x})\; (-)^{m+t'}\, C^{\nu\;1\;\alpha}_{0\;0}\, C^{\ell'\;1\;\nu}_{0\;0}\, C^{\nu\;\;\;1\;\;\alpha}_{-(m'+s')\;t'}\, C^{\ell'\;1\;\nu}_{-m'\;-s'}$$

$$(\mathrm{x})\; (\rho' M+m | d^{\alpha}_{0,-(m'+s')+t'} | \rho M)\, \delta_{m+t',\, m'+s'} \Big\} .$$

The integral $(\underline{\varrho}M \,|\, d^{l}_{0,-m} \,|\, \underline{\varrho}'M')$, like the integral F in Chapter V, is

$$(\underline{\varrho}M|d^{l}_{0,-m}|\underline{\varrho}'M') \cong \frac{(-)^{m}}{2\eta} G^{l}_{m0} \sum_{s} g^{l}_{m0}(s) \left(\frac{1}{4\eta}\right)^{s+\frac{m}{2}} \mathcal{S}_{\underline{\varrho}\underline{\varrho}'} , \tag{J.5}$$

where $\mathcal{S}_{\underline{\varrho}\underline{\varrho}'}$ is known (see (5.37)) and gives the selection rule for

in a rather complicated way.

The higher order terms in $\bar{V}_{\alpha\alpha'}$ may be treated in a similar manner although the amount of labor involved is expected to rapidly become prohibitive.

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