

## SCATTERING OF NEUTRONS BY MOLECULES WITH LARGE ENERGY TRANSFER

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The scattering of neutrons by molecules is treated on the assumption that the energy transferred in a collision is much greater than the average separation of vibrational energy levels of the molecule. It is shown that then the expression for the differential cross section (in energy and angle) can be expressed in terms of a few simple terms in an expansion, which are then averaged over the orientations of the molecule. In the approximation given by the leading term of the expansion, some other important scattering characteristics have been found. The formulas apply to any molecule. For certain types of molecules the final expressions for the scattering cross section are reduced to single integrals, and can be easily evaluated numerically. Results of computations for water are given.

**D**URING the collision of a neutron with a nucleus in a molecule, the chemical binding of the atoms plays an important role. In general the scattering cross section is a complicated function, depending on the properties of the molecule and the structure of its energy levels. The high energy region is important for neutron scattering because this dependence is not so detailed, and one can achieve a compact as well as quite complete mathematical description.

The range of neutron energies and energy transfers in the collision considered here is of the order of a few electron volts, which is much greater than the separation of vibrational levels of the molecule. The scattering of such neutrons may be accompanied by quite complex intramolecular transformations: excitation of high energy levels and dissociation of the molecule. The problem is greatly simplified if we disregard the final state of the molecule. Then only the parameters of the neutron which is being scattered are fixed, and one can use the convenient and well-developed formalism described in papers of Placzek,<sup>[1]</sup> Wick,<sup>[2]</sup> and Zemach and Glauber.<sup>[3]</sup> Such a formulation of the problem, which we shall also use here, is most interesting for studies of the behavior of neutrons in moderating media, and is most convenient for studying the properties of the molecules themselves.

The basic formal results for the scattering of neutrons in the approximation of the Fermi pseudopotential were already found by Placzek for systems of heavy nuclei, and by Wick, who generalized the method to apply to light nuclei. But these results are useful only for getting the total scattering cross section, the mean energy loss and other

energy moments, which of course does not give a complete picture of the scattering. In the first section of the present paper, we give a further extension of the Placzek-Wick method to the double-differential cross section (in energy and angle) and to other characteristics of the scattering which cannot be gotten by the method described in <sup>[1,2]</sup>.

In the second and third sections, after justification, the method is applied to the scattering of neutrons by molecules. The scattering of neutrons by molecules has been studied in many papers,<sup>[3-5]</sup> but with respect to the double differential cross section only individual features of the problem can be regarded as understood. Zemach and Glauber gave a solution of the problem of scattering by a system of oscillators and by a rotator separately. The problem of the rotator and the rigid molecule has also been treated by Krieger and Nelkin and by Volkin.<sup>[4,5]</sup> As applied to molecules, the oscillator model is applicable only to heavy molecules, while the rotator model can be used for any molecule, but only for energies where there are no vibrational transitions. The combined vibration-rotation effect<sup>1)</sup> including vibrational transitions cannot be gotten simply by superposing the results for oscillators and rotators, since they are disjoint: the rigid molecule model is applicable only when the oscillator model is not valid. For the case of energy transfer which is large compared to the difference between vibrational energy levels, the method described here gives a solution of this

<sup>1)</sup>Zemach and Glauber<sup>[2]</sup> treated this effect by a method similar to that of Wick, and consequently not applicable for our purposes.

problem in the most general form.

In the third section we also discuss the effect of averaging the scattering over all orientations of the molecule. For the case of thermal motion (where the incident energy, unlike our case, is thermal) the averaging is usually done approximately,<sup>[4]</sup> which spoils the accuracy of the results. In the present paper, in addition to formulas which are approximate in this sense, we also, for a certain class of molecules, give rigorous formulas obtained on the basis of an exact averaging of the scattering over the molecular orientations.

## 1. GENERAL TREATMENT OF THE SCATTERING PROBLEM

The differential cross section for scattering of neutrons by a system of atoms, when we neglect interference terms is given by the sum of the cross sections for scattering by the individual atoms, which are determined by the following expression<sup>[3]</sup> (where we use the system of units having  $\hbar = 1$ ):

$$\frac{d^2\sigma_\nu}{d\epsilon d\sigma} = \sigma_\nu(\boldsymbol{\kappa}, \epsilon) = a_\nu^2 \frac{k}{2\pi k_0} \int_{-\infty}^{\infty} e^{-i\epsilon t} \langle e^{iH'_\nu t} e^{-iHt} \rangle dt. \quad (1)$$

Here  $a_\nu$  is the scattering length from a rigidly bound atom;  $\mathbf{k}_0$  and  $\mathbf{k} = \mathbf{k}_0 - \boldsymbol{\kappa}$  are the momentum of the neutron before and after scattering;  $\epsilon = k_0^2/2m - k^2/2m$  is the energy transfer,  $m$  is the mass of the neutron,  $\sigma$  the solid angle into which the neutrons are scattered;  $H$  is the Hamiltonian of the scattering system,  $H'_\nu$  the transformed Hamiltonian, which is related to  $H$  by the relation

$$H'_\nu = e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu} H e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu}, \quad (2)$$

$\mathbf{r}_\nu$  is the position vector of nucleus  $\nu$ . The brackets in (1) denote a quantum mechanical average and an average over the Gibbs statistical ensemble.

We write the Hamiltonian of the system in general form:

$$H = \sum_{\mu} p_{\mu}^2/2M_{\mu} + V; \quad (3)$$

then from (2) we have

$$H'_\nu = H + \boldsymbol{\kappa}^2/2M_\nu + L_\nu, \quad L_\nu = \boldsymbol{\kappa}\cdot\mathbf{p}_\nu/M_\nu. \quad (4)$$

We use Wick's<sup>[2]</sup> operator expansion:

$$e^{iH'_\nu t} e^{-iHt} = e^{it\boldsymbol{\kappa}^2/2M_\nu} \sum_{n=0}^{\infty} \frac{(it)^n}{n!} g_n(\boldsymbol{\kappa}), \quad (5)$$

in which the expansion coefficients are given by the following recursion relation:

$$g_{n+1} = g_n L_\nu + n g_{n-1} [H, L_\nu] + \frac{1}{2} n(n-1) g_{n-2} [H, [H, L_\nu]] + \dots \quad (6)$$

We note that the various commutators are repeated in each coefficient  $g_n$ . Combining these repeated commutators by using (6), we write the expression for  $g_n$  in the form

$$g_n = L_\nu^n + \frac{1}{2} n(n-1) L_\nu^{n-2} [H, L_\nu] + \frac{1}{6} n(n-1)(n-2) L_\nu^{n-3} \{[H, L_\nu], L_\nu\} + [H, [H, L_\nu]] + \frac{1}{8} n(n-1)(n-2)(n-3) L_\nu^{n-4} \times [H, L_\nu] [H, L_\nu] + \dots \quad (7)$$

In (7) we have dropped the commutators

$$[H, [H, [H, L_\nu]]] \quad (8)$$

and those of higher order in  $H$ . We shall treat only the terms given in (7), since for the case of large energy transfer the contribution of the omitted terms to the final result will be negligible.

We now substitute (7) into (5) and (5) into (1), and sum the expression over  $n$  and integrate over  $t$ ; we then have an expression for the differential cross section:

$$\begin{aligned} \sigma_\nu(\boldsymbol{\kappa}, \epsilon) = & a_\nu^2 \frac{k}{k_0} \left\langle \delta \left( \frac{\boldsymbol{\kappa}^2}{2M_\nu} - \epsilon + L_\nu \right) \right. \\ & + \frac{1}{2} \delta^{(2)} \left( \frac{\boldsymbol{\kappa}^2}{2M_\nu} - \epsilon + L_\nu \right) [H, L_\nu] \frac{1}{8} \delta^{(3)} \left( \frac{\boldsymbol{\kappa}^2}{2M_\nu} - \epsilon + L_\nu \right) \\ & + \{[H, L_\nu], L_\nu\} + [H, [H, L_\nu]] \} \frac{1}{8} \delta^{(4)} \left( \frac{\boldsymbol{\kappa}^2}{2M_\nu} - \epsilon + L_\nu \right) \\ & \left. + [H, L_\nu] [H, L_\nu] + \dots \right\rangle. \quad (9) \end{aligned}$$

We introduce the quantity  $p_{\nu 0}$ , which is a characteristic momentum of the scattering atom, and estimate the terms containing derivatives of the  $\delta$  function. Averaging the term containing the  $s$ -th derivative gives a quantity of order  $(M_\nu/\kappa)^{s+1} F/p_{\nu 0}^s$ , where  $F$  gives the order of magnitude of the corresponding commutator. Considering the structure of the commutators appearing in (9), we can already conclude from such a rough estimate of the terms in (9) that this series converges in the small parameter  $p_{\nu 0}/\kappa$  of our problem; we can also assert that the second and third terms are of the same order, that the fourth and fifth terms give higher order corrections, and that the term containing the commutator (8) [which enters into (7) together with the factor  $L_\nu^{n-5}$ ] should be a correction term for the whole expression (9).

Let us look at the individual terms of (9) in more detail. The first one corresponds to the

“impulse” approximation:<sup>2)</sup> the neutrons are scattered from free nuclei having the same momentum distribution as they have in the initial state of the scattering system. The limiting transition  $\epsilon, \kappa^2/2M_\nu \rightarrow \infty$  is immediately carried out and gives the scattering by free nuclei which were initially at rest. In the “impulse” approximation, the collision of the neutron and nucleus is treated classically, but the properties exhibited by the system in scattering are quantum mechanical. For example, when the temperature of the medium  $T \rightarrow 0$ , formula (9) does not give the classical limit.

The other terms in (9) represent corrections to the “impulse” approximation due to the influence of binding on the nuclear recoil. The corrections are not as simple as the first term, but using them greatly improves the result and extends the range of energies.

Formula (9) gives the double differential cross section, but it can be used to get other important characteristics of the scattering: angular moments of the function (9), including the cross section for a given energy transfer  $d\sigma/d\epsilon$  for  $\epsilon > E_{\text{syst}}$ , as well as the cross section for scattering of neutrons at large angles. Because of the restriction on the energy transfer, the integration over  $\epsilon$  in (9) for small angles gives an incorrect result. For this reason, one also gets an incorrect result for the total cross section (to be precise, small corrections to the geometrical cross section are not taken into account correctly; these can be gotten from the formulas of Placzek<sup>[1]</sup> and Wick<sup>[2]</sup>). But formula (9) does permit us with sufficient accuracy to include the influence of chemical binding on the total scattering cross section in the energy range where  $\epsilon > E_{\text{syst}}$  (where  $E_{\text{syst}}$  is a characteristic energy of the system,  $E_{\text{syst}} \sim p_{\nu 0}^2/2M_\nu$ ).

## 2. SCATTERING OF NEUTRONS BY MOLECULES. GENERAL FORMULAS.

The usual picture of a molecule is based on a model consisting of point atoms coupled by forces which keep the atoms near their equilibrium positions; these positions correspond to deep minima in the potential energy, so that from the classical point of view the atoms vibrate with amplitudes which are small compared to the dimensions of the molecule. Corresponding to this picture, in quantum mechanics the condition

$$\Delta \bar{E}_r \ll \bar{\omega}, \quad (10)$$

<sup>2)</sup>This terminology, which is taken from Goldanskiĭ,<sup>[6]</sup> fits the physics of the phenomenon.

is well satisfied ( $\Delta \bar{E}_r$  and  $\omega$  are the mean separations of rotational and vibrational levels, respectively, and  $\bar{\omega}$  is usually of the order of some tenths of eV).

As already stated, we are considering the range of energy transfers of the order of several eV. Then the nuclear recoil velocity is much less than the electron velocities, i.e., it is still not high enough to seriously perturb the electron motion. Thus the requirement of adiabaticity (the possibility of splitting the wave function into an electronic and a nuclear part) for the initial and final states is generally reasonable. But if we are studying the details of processes with large energy transfer, this requirement can be weakened considerably. A process with large energy transfer occurs in a time  $\tau \sim 1/\epsilon$  which is much less than the vibrational periods of the molecule. Those nonadiabaticities which result in electronic transitions (which are effective only if there are surfaces of crossing of terms) and which involve times of the order of a few molecular vibration periods cannot manifest themselves in scattering, and have no effect in either the “impulse” approximation or the leading corrections to it. In other words, the requirement of adiabaticity of the final state of the molecule is unnecessary. Thus if the electronic state of the initial molecule is separated from the nuclear state, it need not be included any further, and we can use just that part of the Hamiltonian which acts on the coordinates of the nuclei; we note that the most general form of this part of the Hamiltonian is given by (3).

In order to use formula (9) directly, we need the condition

$$\kappa \gg p_{\nu 0} \quad (p_{\nu 0} = \sqrt{M\bar{\omega}}), \quad (11)$$

which can also be rewritten in the form  $1/\kappa a_0 \ll 1$ , where  $a_0$  is the amplitude of vibration of the atoms in the molecule  $\sim 10^{-9}$  cm.

Formula (9), which was obtained neglecting interference terms, includes terms of order  $1/\kappa a_0$  (first order correction) and  $(1/\kappa a_0)^2$  (second order quantum correction). The interference terms give a contribution to the differential cross section of order<sup>3)</sup>  $a_{\text{coh}}^2/a_{\text{inc}}^2 \kappa b$  ( $a_{\text{coh}}$  and  $a_{\text{inc}}$  are the coherent and incoherent scattering amplitudes;  $b$  is the interatomic distance  $\sim 10^{-8}$  cm),

<sup>3)</sup>Such a contribution appears only when the molecule contains atoms with equal or almost equal masses. The interference from two different atoms is effective only if  $\kappa^2/2M_1 - \kappa^2/2M_2 \lesssim \bar{\omega}$ . If this is not the case, the matrix elements for the scattering from different atoms differ from zero in non-overlapping energy regions and the interference is completely negligible.

which is a fraction  $1/10 a_{\text{coh}}^2/a_{\text{inc}}^2$  of the contribution of the first quantum correction in (9). Usually  $a_{\text{coh}}^2/a_{\text{inc}}^2 \sim 1$ , but there are exceptions. For example, for molecules containing hydrogen, when there is no correlation between the proton spins,  $a_{\text{coh}}^2/a_{\text{inc}}^2 \approx 1/40$  (cf., for example, p. 442 of [7]). It follows that formula (9), including the first and sometimes even the second order quantum corrections, can be used for a description of the actual picture of neutron scattering by molecules.

When we make the additional assumption that the vibrational and rotational motions are independent, the total energy operator (3) takes the form  $H = H_t + H_r + H_v$  and includes the translational motion of the molecule as a whole, the rigid-body rotation of the molecule and the vibrational energy of the nonrotating molecule.

Let the equilibrium position of atom  $\nu$  be given by the vector  $\mathbf{b}_\nu$ ; then the vector displacement  $\mathbf{r}_\nu$  of the atom from its equilibrium position is made up of independent contributions from each of the types of motion:

$$\mathbf{r}_\nu = \mathbf{r}_t + \mathbf{r}_r + \mathbf{r}_v \quad (12)$$

If the molecule has a rigid-body rotational velocity  $\Omega$ , the velocity of an atom in the molecule can be written as

$$\mathbf{v}_\nu = \mathbf{V}_m + [\Omega \mathbf{b}_\nu] + \mathbf{v}_\nu^v \quad (13)^*$$

where  $\mathbf{v}_\nu^v$  is the velocity vector in the moving frame and is associated only with the vibrational motion of the molecule;  $\mathbf{V}_m$  is the velocity of the molecule.

The internal motion of an  $N$ -atom molecule is described by  $3N-6$  ( $3N-5$  for linear molecules) independent normal coordinates,

$$H_v = \frac{1}{2} \sum_i (P_i^2 + \omega_i^2 Q_i^2), \quad (14)$$

and the displacement of the atom in the rotating system is

$$\mathbf{r}_\nu^v = \sum_i c_i^r Q_i; \quad \mathbf{v}_\nu^v = \sum_i c_i^v P_i, \quad (15)$$

where  $c_i^r$  is the vector amplitude,  $P_i$  the moment conjugate to the normal coordinate  $Q_i$ .

After introducing the normal coordinates, the wave function of the molecule has the form

$$\psi = \psi_t \psi_r \prod_i \psi_i(Q_i). \quad (16)$$

In averaging the operators in (9) which, we recall, is to be done in both the quantum mechanical and statistical sense, we shall keep in mind that,

\* $[\Omega \mathbf{b}_\nu] = \Omega \times \mathbf{b}_\nu$ .

because of condition (10), since the parameter  $\bar{\omega}/\bar{\epsilon}$  is assumed to be small, the rotational transitions can be treated classically. The classical approximation for a rotator means that there is no change in orientation during the time of collision of the molecule, and we can replace the rotational wave function by a wave packet with simultaneously assigned orientation and angular momentum.<sup>[4]</sup>

After this is done, the averaging in (9) reduces to an integration over the angular momentum  $l$  including the Boltzmann temperature factor  $\exp(-1 \cdot I^{-1} \cdot 1/2T)$  followed by an average over the orientations of the molecule ( $T$  is the temperature of the medium in the system of units with the Boltzmann constant  $k_B = 1$ ;  $I$  is the moment of inertia tensor of the molecule).

The classical approximation for the rotator also means that the operators describing the rotational motion are not contained in the commutators in formula (9). Using (14) and (15), we can write for the commutators (we include only the first correction to the "impulse" approximation)

$$[H, L_\nu] = -\frac{1}{i} \sum_j (\kappa c_j^r) \omega_j^2 Q_j; \quad [[H, L_\nu], L_\nu] = -\sum_j (\kappa c_j^r)^2 \omega_j^2. \quad (17)$$

We now split the  $\delta$  function and its derivatives, which appear in (9), into factors containing separate independent variables (we use (13) and (15)):

$$\begin{aligned} \delta^{(s)}(E - \kappa \mathbf{v}_\nu) &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \delta(E_t - \kappa \mathbf{V}_m) \\ &\times \delta(E_r - [\Omega \mathbf{b}_\nu] \kappa) \delta^{(s)}(E_j - \kappa c_j^r P_j) \\ &\times \prod_{i \neq j} [\delta(E_i - \kappa c_i^r P_i) dE_i] dE_t dE_r dE_j \\ &\times \delta(E - E_t - E_r - \sum_i E_i) \end{aligned}$$

and bring the expression for the differential cross section to the form

$$\begin{aligned} \sigma_\nu(\kappa, \epsilon) &= a_\nu^2 \frac{k}{k_0} \left\langle \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} W_t(E_t) W_r(E_r) \right. \\ &\times \left\{ \prod_i [W_i(E_i) dE_i] \sum_j W_j^{(1)} \prod_{i \neq j} [W_i(E_i) dE_i] dE_j \right\} \\ &\times dE_t dE_r \delta(E - E_t - E_r - \sum_i E_i) \rangle_{\Omega_{\text{mol}}}. \quad (18) \end{aligned}$$

The factor which takes account of the excitation of rotational degrees of freedom has the form

$$W_r = N_r \int \exp(-I^{-1} 1/2T) \delta(E_r - [\Omega \mathbf{b}_\nu] \kappa) dl$$

( $N_r$ , and  $N_t$  and  $N_n^i$  later on, are normalization

factors whose meaning is obvious). The integration is done as in [4]; we get

$$W_r = \left( \frac{1}{2\pi T \kappa R_{\nu \kappa}} \right)^{1/2} \exp \left( - \frac{E_r^2}{2T \kappa R_{\nu \kappa}} \right). \quad (19)$$

The tensor  $R_{\nu}$ , which was introduced in [4], is related to the moment of inertia of the molecule and the position of the scattering atom relative to the center of gravity of the molecule.

The integration of the factor for translational motion

$$W_t = N_t \int \exp(-MV_m^2/2T) \delta(E - \kappa V_m) dV_m$$

is done by elementary methods, giving

$$W_t = \left( \frac{M}{2\pi T \kappa^2} \right)^{1/2} \exp \left( - \frac{ME_t}{2T \kappa^2} \right). \quad (20)$$

In (19) and (20) the rotational and translational transitions are included classically. For the vibrational degrees of freedom we have factors of the type

$$W_i = \langle \delta(E_i - \kappa c_i^j P_i) \rangle,$$

$$W_i^{(1)} = \left\langle \frac{1}{2} \delta^{(2)}(E_i - \kappa c_i^j P_i) \kappa c_i^j \omega_i^2 \left( -\frac{1}{i} Q_i \right) + \frac{1}{6} \delta^{(3)}(E_i - \kappa c_i^j P_i) (\kappa c_i^j)^2 \omega_i^3 \right\rangle. \quad (21)$$

The average of the operators in (21) can be expanded in the form

$$\langle A_i \rangle = \sum_n N_n^i e^{-n\omega_i/T} \langle \Psi_n^i | A_i | \Psi_n^i \rangle, \quad (22)$$

where the operators under the summation sign are averaged over harmonic oscillator wave functions, which in the momentum representation (which makes the averaging easier) have the form

$$\Psi_n^i = (2^n n! \sqrt{\pi \bar{\omega}_i})^{-1/2} H_n(P_i / \sqrt{\bar{\omega}_i}) e^{-P_i^2/2\bar{\omega}_i}, \quad (23)$$

where the  $H_n(x)$  are Hermite polynomials.

Using the Bloch formula for the momentum distribution of the oscillator (cf. for example, [18], p. 107)

$$\Phi_B^i = \sum_n N_n^i e^{-n\omega_i/T} [\Psi_n^i(P_i)]^2 = \left( \pi \bar{\omega}_i \operatorname{cth} \frac{\bar{\omega}_i}{2T} \right)^{-1/2} \exp \left( - \frac{P_i^2}{\bar{\omega}_i \operatorname{cth}(\bar{\omega}_i/2T)} \right), \quad (24)^*$$

we can perform the sum over  $n$  in (22).

First we note the following property of the functions (23):

$$\left\langle \Psi_n^i \left| \frac{1}{i} Q_i \right| \Psi_n^i \right\rangle = \frac{1}{2} \frac{d}{dP_i} [\Psi_n^i(P_i)]^2.$$

\*cth = coth

Also using (24) and (21), we find

$$W_i = \int \Phi_B^i \delta(E_i - \kappa c_i^j P_i) dP_i; \quad W_i^{(1)} = -\frac{1}{12} \int \Phi_B^i(P_i) \delta^{(3)}(E_i - \kappa c_i^j P_i) (\kappa c_i^j)^2 \omega_i^2 dP_i,$$

and after integrating, we finally get for (21)

$$W_i = \frac{1}{\sqrt{\pi} \alpha_i} \exp(-E_i^2/\alpha_i^2) \quad \left( \alpha_i = (\kappa c_i^j)^2 \omega_i \operatorname{cth} \frac{\bar{\omega}_i}{2T} \right), \quad (25)$$

$$W_i^{(1)} = \frac{1}{3\sqrt{\pi}} \frac{(\kappa c_i^j \omega_i)^2}{\alpha_i^2} E_i [2E_i^2/\alpha_i^2 - 3] \exp(-E_i^2/\alpha_i^2). \quad (26)$$

We note that  $W_r$  and  $W_t$  have the same form as  $W_i$  in (25).

Because of the simplicity of the expressions in (19), (20), (25) and (26), it is easy to carry out the integration in (18) over the variables  $E_r$ ,  $E_t$  and  $E_i$ . As a result we get the following expression for the differential cross section:

$$\sigma_v(\kappa, \varepsilon) = a_v^2 \frac{k}{k_0} \left\langle \frac{1}{\sqrt{\pi} \alpha} \left\{ 1 + \frac{1}{3\alpha^2} \sum (\kappa c_i^j)^2 \omega_i^2 \frac{E}{\alpha} \left[ 2 \frac{E^2}{\alpha^2} - 3 \right] \right\} e^{-E^2/\alpha^2} \right\rangle_{\Omega_{\text{mol}}}, \quad (27)$$

where

$$\alpha^2 = \sum (\kappa c_i^j)^2 \omega_i \operatorname{cth} \frac{\bar{\omega}_i}{2T} + 2T(\kappa R_{\nu \kappa} + \kappa^2/M);$$

$$E = \varepsilon - \kappa^2/2M_v. \quad (28)$$

Formula (27) is general and makes only two assumptions: (16) and the assumption that the electronic state of the initial molecule is separable from the nuclear state (both these assumptions are usual in applications). The further steps of averaging over molecular orientation require more specific information about the molecules. We introduce the quantities  $\bar{\alpha}^2 = \kappa^2 \bar{\omega}/M_v$ ,  $\Sigma(\kappa \cdot c_{\nu}^i)^2 \omega_i^2 = \kappa^2 \bar{\omega}^2/M_v$  averaged over orientation, and consider the question of the accuracy of the expressions we have obtained. One can see that the corrections to the "impulse" approximation given in (27) are of order

$$\frac{1}{3\sqrt{2\bar{\omega}/\bar{\omega}}} \frac{\bar{\omega}^2}{\bar{\omega}^2} \left( \frac{E^2}{\alpha^2} \right)^{1/2} [2E^2/\alpha^2 - 3],$$

where  $\bar{\omega}$  is the average energy loss for a given  $\kappa$  ( $\bar{\omega} = \kappa^2/2M_v$ ).

In the region of the maximum for the process, up to values  $E^2/\alpha^2 \approx 2$ , where the cross section is down by about a factor of ten, the corrections give a contribution somewhat less (factor of three) than  $(\bar{\omega}/\bar{\varepsilon})^{1/2}$ , and one can show that this remains true in the higher corrections to the "impulse" approximation; thus we can state that over a quite wide range around the maximum for the process formula (27) reproduces the cross section to an

accuracy of the order of  $1/10 (\bar{\epsilon}/\bar{\omega})^{-1}$ . One can also see that in regions far from the maximum, the conditions for the validity of (27) are much poorer.

With increasing temperature, the relative importance of the corrections decreases. This is natural: from the classical point of view the case we are considering gives the optimum conditions.

Formula (9) permits us to find the second quantum correction to (27). However, it is much more complicated and of no practical interest when  $\bar{\epsilon} \gg \bar{\omega}$ .

Using (27) we can get the integral characteristics of the scattering which were mentioned in the first section. We shall be interested in the cross section for scattering with a given energy transfer  $d\sigma/d\epsilon$  (or  $d\sigma/dk$ ), which is very important in applications, and also in the total cross section for scattering with an energy transfer exceeding some minimum value  $D > \bar{\omega}$ . We first note that the corrections vary in sign and furthermore that the main contribution to the integral comes from the region of the maximum, where the corrections are small. Thus we may expect that the integral characteristics are given quite accurately by the "impulse" approximation.

Let us make use of the formal analogy between the expressions obtained on the "impulse" approximation and the formulas for the scattering of neutrons by monatomic gases (cf., for example, [9]). Making the analogous change of variables, we have for  $d\sigma/dk$  in the "impulse" approximation

$$\begin{aligned} \frac{d\sigma}{dk} = \sigma_v \frac{(M_v + m)^2}{4M_v m} \frac{k}{k_0^2} & \left\langle \exp\left(\frac{k_0^2}{\alpha_0^2} - \frac{k^2}{\alpha_0^2}\right) \operatorname{erf}\left(\gamma \frac{k_0}{\alpha_0} - \eta \frac{k}{\alpha_0}\right) \right. \\ & + \operatorname{erf}\left(\gamma \frac{k}{\alpha_0} - \eta \frac{k_0}{\alpha_0}\right) \left[ \exp\left(\frac{k_0^2}{\alpha_0^2} - \frac{k^2}{\alpha_0^2}\right) \operatorname{erf}\left(\gamma \frac{k_0}{\alpha_0} + \eta \frac{k}{\alpha_0}\right) \right. \\ & \left. \left. - \operatorname{erf}\left(\gamma \frac{k}{\alpha_0} + \eta \frac{k_0}{\alpha_0}\right) \right] \right\rangle_{\Omega_{\text{mol}}}, \quad (29) \end{aligned}$$

$\sigma_v = 4\pi a_v^2 M_v^2 (m + M_v)^2$  is the total cross section for scattering by the free atom at rest;  $\alpha_0^2 = M_v^2 \alpha^2 / \kappa^2$ ,  $\alpha^2$  is defined in (28);

$$\eta = \frac{1}{2} \left( \sqrt{\frac{M_v}{m}} - \sqrt{\frac{m}{M_v}} \right), \quad \gamma = \frac{1}{2} \left( \sqrt{\frac{M_v}{m}} + \sqrt{\frac{m}{M_v}} \right),$$

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

Formula (29) is applicable for  $(k_0 - k)^2/2m > \bar{\omega}$ . Let us go into more detail for molecules containing hydrogen. An interesting feature of the scattering of neutrons by bound hydrogen atoms is that the cross section  $d\sigma/dk$  has a characteristic simple form:

$$\frac{d\sigma}{dk} = \sigma_H \frac{2k}{k_0^2} J(k), \quad J(k) = \left\langle \operatorname{erf} \frac{k}{\alpha_0} \right\rangle_{\Omega_{\text{mol}}}, \quad (30)$$

which permits us to draw a number of important conclusions.

1. The effects of chemical binding are important for  $< 1/\alpha_0 > k \sim 1$  and do not disappear as  $k_0 \rightarrow \infty$ . For  $< 1/\alpha_0 > k \ll 1$ , the cross section is  $d\sigma/dk = 2\sigma_H k/k_0^2$  and corresponds to scattering by a free proton at rest.

2. For  $< 1/\alpha_0 > k \ll 1$ , the function  $J(k) = 2 < 1/\alpha_0 > k/\sqrt{\pi}$ . If the scattering is accompanied by intramolecular transformations which have an energy threshold  $D$  (this is just the situation for the dissociation of the molecules), we immediately get for the total cross section of the process near threshold

$$\sigma = \frac{2}{3} \sqrt{\frac{2}{\pi}} \sigma_H \left\langle \frac{\sqrt{m}}{\alpha_0} \right\rangle_{\Omega_{\text{mol}}} \frac{[E_0 - D]^{3/2}}{E_0}, \quad (31)$$

where  $E_0$  is the energy of the incident neutron.

3. The proportionality of the cross section  $d\sigma/dk$  to the factor  $kJ(k)$  is retained for any nonmonochromatic beam of incident neutrons with  $E_0 \gg \bar{\omega}$ .

Integrating (30), we get the total cross section for scattering of neutrons in the energy range for which  $\epsilon > D$ :

$$\sigma = \sigma_H \left\langle \frac{\alpha_0^2}{k_0^2} \left[ \left( \frac{k'^2}{\alpha_0^2} - 1 \right) \operatorname{erf}\left(\frac{k'}{\alpha_0}\right) + \frac{2}{\sqrt{\pi}} \frac{k'}{\alpha_0} e^{-k'^2/\alpha_0^2} \right] \right\rangle_{\Omega_{\text{mol}}}, \quad (32)$$

$k'$  is the momentum of the neutron after scattering corresponding to  $\epsilon = D (k' = \sqrt{2m(E_0 - D)})$ . For  $k' < 1/\alpha_0 > > 1$ , the rigorous averaging over molecular orientations is superfluous. We can simply replace  $\alpha_0^2$  in (32) by  $\bar{\alpha}_0^2$ , its average over orientations.

The general formulas (27) and (29)–(32) contain the dependence on the main characteristics of the molecules: the frequencies  $\omega_i$  and the vector amplitudes, their absolute values and their spatial distribution in the molecules. The  $c_{ij}^1$  contain the force constants of the molecules. Thus information about neutron scattering in the high-energy region can give additional information about the properties of polyatomic molecules, as already pointed out by Gol'danskiĭ.<sup>[6]</sup> We see that the main advantage of the high energy region is that the results are not complicated by those specific features which are introduced by the various possible final states of the molecule. In other words the advantage is the relatively simple analysis of the experimental material.

We note still another important application of the results. As we see from (29) and particularly

from (30), chemical binding is important for the scattering in a range of energies which is narrow but very important for the physics of moderation of neutrons: because of this region ( $k \sim \sqrt{M\bar{\omega}}$ ) which, expressed in temperature units  $T$ , amounts to a few tenths of a unit, there is a connection between the neutrons which are slowing down and the neutrons of the thermal group.

**3. AVERAGING THE EFFECT OF SCATTERING OVER THE ANGULAR ORIENTATIONS OF THE MOLECULE**

Formulas (27) and (29) require an averaging of the effect of neutron scattering over the molecular orientations. For molecules of arbitrary structure one can give no single recipe for carrying this out. The approximate averaging, in which one replaces  $\alpha^2$  and  $\alpha_0^2$  by  $\bar{\alpha}^2$  and  $\bar{\alpha}_0^2$  (their averages over orientation), does not give the correct result for the double differential cross section but can be used for getting approximate expressions for the cross sections  $d^2\sigma/d\epsilon d\omega d\sigma/dk$  (as can be seen from the tables given later). In obtaining rigorous results, it is most convenient to choose the coordinate system fixed in the molecule so that the tensor  $R_\nu$  is diagonal. In diagonal form,  $R_\nu$  has components  $(r_1, r_2, 0)$ ;  $r_1$  and  $r_2$  are given in [5]. The zero component corresponds to the axis passing through the center of gravity of the molecule and the scattering atom.

For certain important types of molecules, formulas (27) and (29) can be written in terms of relatively simple integral expressions.

a) Linear and diatomic molecules. The vibrations of a diatomic molecule are along the line of the nuclei, and those of a linear molecule are either along the axis of the molecule or in a plane perpendicular to it. We choose our coordinate system so that one of the axes coincides with the axis of the molecule. In such a coordinate system the tensor  $R_\nu$  is diagonal, and its components for nucleus  $\nu$  are equal to  $r_1 = r_2 = r = \Gamma^{-1} b_\nu^2$  (where  $I$  is the moment of inertia of the molecule).

We introduce effective "frequencies" for longitudinal and transverse vibrations  $\omega_{||}$  and  $\omega_{\perp}$  in accordance with the following form for  $\alpha^2$ :

$$\alpha^2 = (\kappa^2/M_\nu) [\omega_{||} \cos^2\theta + \omega_{\perp} \sin^2\theta], \tag{33}$$

where  $\theta$  is the angle between the molecular axis and the vector  $\kappa$ . Similarly we introduce

$$\frac{1}{\omega_{||}^2} \sum_i (\kappa c_i^x)^2 \omega_i^2 = \frac{\kappa^2}{M_\nu} [A \cos^2 \theta + B \sin^2 \theta]. \tag{34}$$

We write  $\rho = (\epsilon - \kappa^2/2M_\nu)/\kappa\sqrt{\omega_{||}/M_\nu}$  and change to dimensionless variables, in which the energies

are given in units of  $\omega_{||}$  and the momenta in units of  $\sqrt{2M_\nu\omega_{||}}$  ( $\rho = (\epsilon - \bar{\epsilon})/\sqrt{2\bar{\epsilon}}$ ). Integrating (27) over the orientations of the molecule, using (33) and (34), we get for the differential cross section for neutron scattering

$$\sigma_\nu(\kappa, \epsilon) = a_\nu^2 \frac{k}{k_0} \left[ \frac{M_\nu}{\pi \kappa^2 \omega_{||}} \right]^{1/2} \left[ f(\rho) + \frac{1}{3\sqrt{2\epsilon}} \varphi(\rho) \right], \tag{35}$$

where

$$f(\rho) = \frac{\beta}{2\sqrt{\beta-1}} \int_1^\beta e^{-\rho^2 t} \frac{dt}{t\sqrt{\beta-t}}; \quad \beta = \omega_{||}/\omega_{\perp};$$

$$\varphi(\rho) = \frac{\beta}{2\sqrt{\beta-1}} \rho \int_1^\beta e^{-\rho^2 t} \frac{(2\rho^2 t - 3)}{\sqrt{\beta-t}} [B\beta + (A - B\beta) \frac{\beta-t}{\beta-1}] dt. \tag{36}$$

In general the integrals (36) cannot be expressed in terms of elementary functions. But in the frequently occurring case where the transverse vibrations are much weaker than the longitudinal ones, for not too high temperature  $\beta \gg 1$ ,  $A \gg B$  and the functions (36) for  $\rho^2\beta \gg 1$  can be written in the form

$$f(\rho) = \frac{1}{2} \text{Ei}(-\rho^2),$$

$$\varphi(\rho) = \frac{A}{2\rho} (2\rho^2 - 1) e^{-\rho^2} \quad \left( \text{Ei}(-\rho^2) = - \int_{-\rho^2}^{-\infty} e^t \frac{dt}{t} \right).$$

For  $\rho = 0$ , which corresponds to  $\epsilon = \kappa^2/2M_\nu$ ,

$$f(0) = \frac{1}{2} \sqrt{\frac{\beta}{\beta-1}} \ln \frac{\sqrt{\beta} + \sqrt{\beta-1}}{\sqrt{\beta} - \sqrt{\beta-1}}; \quad \varphi(0) = 0.$$

For the cross section (30), expressed in dimensionless momentum variables ( $p = k/\sqrt{2m\omega_{||}}$ )

$$\frac{d\sigma}{dp} = \sigma_H \frac{2\rho}{\rho_0^2} J(\rho), \tag{37}$$

the factor  $J(p)$  has the form

$$J(\rho) = \frac{\beta}{2\sqrt{\beta-1}} \int_1^\beta \text{erf}(\rho\sqrt{2t}) \frac{dt}{t^{3/2}\sqrt{\beta-t}}; \tag{38}$$

and we get for  $p \ll 1$ ,

$$J(\rho) = \rho \sqrt{\frac{2}{\pi}} \sqrt{\frac{\beta}{\beta-1}} \ln \frac{\sqrt{\beta} + \sqrt{\beta-1}}{\sqrt{\beta} - \sqrt{\beta-1}}.$$

b) More complex molecules. For complex molecules an interesting case is that in which the system of spatially distributed amplitude vectors forms three mutually perpendicular directions coinciding with the coordinate system in which the tensor  $R_\nu$  is diagonal. The last condition is not necessary at low temperatures. In this case the scattering cross section can again be written in terms of a few integrals.

In accordance with our assumption, we write

**Table I.** Scattering of neutrons by water molecules for  $T \rightarrow 0$  and  $T = 300^\circ \text{K}$  for the case of interaction with one of the hydrogen atoms

$\rho^*$	0	0.05	0.10	0.20	0.30	0.40	0.60	0.80	1.00	1.25	1.50
$T \rightarrow 0$											
$f(\rho)^*$	1.900	1.300	1.070	0.756	0.559	0.431	0.278	0.188	0.123	0.086	0.055
$\varphi(\rho)^*$	0	-2.50	-1.92	-1.101	-0.561	-0.240	0.080	0.201	0.250	0.246	0.225
$T = 300^\circ$											
$f(\rho)^*$	1.642	1.371	1.160	0.869	0.663	0.525	0.345	0.228	0.157	0.102	0.069
$\varphi(\rho)^*$	0	-1.322	-1.441	-1.150	-0.847	-0.501	0.088	0.109	0.198	0.228	0.225

\*Values of the functions  $f(\rho)$  and  $\varphi(\rho)$  of (40) to be used in the cross section (35).

**Table II**

$\bar{\rho}$	0	0.05	0.15	0.25	0.35	0.45	0.60	0.80	1.00
$T \rightarrow 0$									
$J(\rho)^*$	0	0.149	0.426	0.623	0.742	0.830	0.915	0.960	0.980
$J'(\rho)^*$	0	0.125	0.362	0.568	0.729	0.843	0.941	0.988	0.998
$T = 300^\circ$									
$J(\rho)^*$	0	0.130	0.377	0.580	0.730	0.813	0.912	0.975	0.990
$J'(\rho)^*$	0	0.117	0.341	0.539	0.697	0.815	0.922	0.982	0.997

\*Values of the functions  $J(\rho)$  and  $J'(\rho)$  in the formula (37) for the cross section.

$$\alpha^2 = \frac{\kappa^2}{M_v} \omega_{\parallel} [\cos^2 \theta + d \sin^2 \theta \cos^2 \varphi + q \sin^2 \theta \sin^2 \varphi],$$

$$\sum (\kappa c_i^t)^2 \omega_i^2 = \frac{\kappa^2}{M_v} \omega_{\parallel}^2 [A \cos^2 \theta + B \sin^2 \theta \cos^2 \varphi + C \sin^2 \theta \sin^2 \varphi] \quad (39)$$

The significance of the variables  $\theta$  and  $\varphi$  is obvious ( $1 > d \geq q$ ). The integration gives the following result: the scattering cross sections are given by formulas (25) and (30), where

$$f(\rho) = \frac{1}{\pi} \int_1^{1/q} e^{-\rho^2 t} \frac{dt}{t} \times \begin{cases} \frac{1}{\sqrt{(1-d)(1-qt)}} K \left( \sqrt{\frac{d-q}{1-d} \frac{t-1}{1-qt}} \right), & 1 \leq t \leq 1/d, \\ \frac{1}{\sqrt{(d-q)(t-1)}} K \left( \sqrt{\frac{1-d}{d-q} \frac{1-qt}{t-1}} \right), & 1/d < t \leq 1/q; \end{cases}$$

$$\varphi(\rho) = \frac{1}{\pi} \rho \int_1^{1/q} e^{-\rho^2 t} (2\rho^2 t - 3) dt \begin{cases} u_1(t), & 1 \leq t \leq 1/d, \\ u_2(t), & 1/d < t \leq 1/q; \end{cases}$$

$$u_1(t) = \left\{ \frac{B-C}{d-q} + \left[ C - \frac{(B-C)}{d-q} q \right] t \right\} + \frac{1}{\sqrt{(1-d)(1-qt)}} K \left( \sqrt{\frac{d-q}{1-d} \frac{t-1}{1-qt}} \right) + \left( \frac{A-C}{1-q} - \frac{B-C}{d-q} \right) \sqrt{\frac{1-qt}{1-d}} E \left( \sqrt{\frac{d-q}{1-d} \frac{t-1}{1-qt}} \right);$$

$$u_2(t) = \left\{ \frac{B-C}{d-q} + \left[ C - \frac{B-C}{d-q} q \right] t \right\} + \left[ \frac{A-C}{1-q} - \frac{B-C}{d-q} \right] \frac{1-q}{1-d} (1-dt) \times \frac{1}{\sqrt{(d-q)(t-1)}} K \left( \sqrt{\frac{1-d}{d-q} \frac{1-qt}{t-1}} \right) \left( \frac{A-C}{1-q} - \frac{B-C}{d-q} \right) + \sqrt{\frac{d-q}{(1-d)^2} (t-1)} E \left( \sqrt{\frac{1-d}{d-q} \frac{1-qt}{t-1}} \right). \quad (40)$$

$K(x)$  and  $E(x)$  are the complete elliptic integrals of the first and second kind. The function  $J(\rho)$  is obtained from  $f(\rho)$  by replacing the factor  $e^{-\rho^2 t}$  in the integrand by  $\text{erf}(\rho \sqrt{2t})/t^{1/2}$ .

The water molecule. We consider the scattering of neutrons by one of the hydrogen atoms in a water molecule.<sup>4)</sup> We shall assume (this is well justified) that the normal vibrations with frequencies  $\omega_1 = 0.446 \text{ eV}$  and  $\omega_3 = 0.466 \text{ eV}$  are along the line passing through the center of gravity of

<sup>4)</sup>For water molecules this case is of principal interest, since the cross section for scattering by the oxygen atom is ten times less than for scattering by the two hydrogen atoms. Furthermore, because of the large difference in masses, the additional scattering by the oxygen has no effect whatsoever on those features which appear from the scattering by the bound hydrogen atoms.



the molecule and the hydrogen atom (we choose this as the  $z'$  axis). Using the interatomic distance  $r_{\text{O-H}} = 0.97 \text{ \AA}$  and the angle  $105^\circ$  between the O-H bonds, we get  $r_1 = 0.945 \text{ m}^{-1}$  and  $r_2 = 0.481 \text{ m}^{-1}$ . The component  $r_2$  corresponds to rotation in the plane of the molecule. It is therefore clear that in this case formulas (35) and (40) are completely applicable.

Using the known values of the force constants of the  $\text{H}_2\text{O}$  molecule (<sup>[10]</sup>, p. 175) and taking account of the normalization of the  $\mathbf{c}_p^1$ , we find for the amplitude vectors

$$[c_{\text{H}}^{(1)}]^2 = [c_{\text{H}}^{(3)}]^2 = 0.472 \text{ m}^{-1}; [c_{\text{H}}^{(2)}]^2 = 0.464 \text{ m}^{-1}.$$

Because of the importance of the case considered here, we give the values of the parameters  $\omega_{\parallel}$ ,  $d$ ,  $q$  and  $A$ ,  $B$ ,  $C$ , which appear in formulas (39) and (40):

$$\omega_{\parallel} = 0.472 \left[ \omega_1 \text{cth} \frac{\omega_1}{2T} + \omega_3 \text{cth} \frac{\omega_3}{2T} \right] + 0.110 T,$$

$$\omega_{\parallel} d = 0.464 \omega_2 \text{cth} \frac{\omega_2}{2T} + 1.072 T, \quad \omega_{\parallel} q = 2 T,$$

$$\omega_{\parallel}^2 A = 0.472 (\omega_1^2 + \omega_3^2), \quad \omega_{\parallel}^2 B = 0.464 \omega_2^2, \quad C = 0.$$

In Tables I and II we give the results of numerical computations of the functions  $f(\rho)$ ,  $\varphi(\rho)$  and  $J(p)$  for  $T \rightarrow 0$  and  $T = 300^\circ \text{K}$ . For comparison

we also give values of  $J'(p)$ , which is obtained from  $J(p)$  by an approximate averaging over molecular orientations.

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