Spin Correlation Effect on the Slow Neutron Scattering by Polyatomic Molecules with Particular Reference to Methane

Juichiro HAMA and Hiroshi MIYAGI

Faculty of Engineering Science, Osaka University, Toyonaka

Zemach and Glauber's approximation for the nuclear spin correlation effect on the slow neutron scattering by polyatomic gas is studied carefully with particular reference to methane. It is shown that the partial differential incoherent scattering cross section based on the above approximation deviates appreciably from the exact one at low temperature. It is pointed out that the mentioned deviation comes principally from an incorrect treatment of the transition amplitude connected with F-states of methane with failure of the condition of detailed balance.

§ 1. Introduction

Following the correlation function formalism by Zemach and Glauber (ZG),[1] many theoretical studies have been done on the scattering of slow neutrons by gas composed of polyatomic molecules.[2] Among them several approximate theories treated the rotational transitions semi-classically.[3],[4] The other theories took into account the discrete nature of rotational levels.[5],[6] However, the relation of them to the semi-classical treatment was not clear. In a previous paper[7] Hama and Nakamura have obtained exactly an analytical expression for the rotational correlation function for a free spherical rotor. Basing the theory on this exact correlation function, they have shown that the effective mass theory of Sachs and Teller[8] in Krieger and Nelkin's formalism[8] can be derived as a limiting case of short time for the free spherical rotor.

However, these are the uncorrelated theories in which the correlation between the nuclear spin system and the rotational one through statistics of identical nuclei is neglected. This correlation effect was taken into account for spherical and symmetric top molecules by Sinha and Venkataraman (SV).[9] However, their treatment was based on ZG's approximation,[1] which will be described below.

Now, the partial differential incoherent scattering cross section is given by

$$(d^2\sigma/d\Omega d\omega)_{\text{incoh}} = (2\pi)^{-1}(k/k_0) \int_{-\infty}^{\infty} dt e^{-i\omega t} [C^2/s(s+1)] \sum_{\nu\nu'} \chi^{\nu\nu'}, \quad (1\cdot1)$$

$$\chi^{\nu\nu'} = \langle \exp(i\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu(t)) s_\nu \cdot s_{\nu'} \exp(-i\boldsymbol{\kappa}\cdot\boldsymbol{r}_{\nu'}(0)) \rangle, \quad (1\cdot2)$$

if the incident neutron beams are unpolarized. Here we assume the molecule

to contain only one kind of identical nuclei. C is the incoherent scattering length of the identical nuclei, r_ν the position vector of the ν-th nucleus, s_ν the ν-th nuclear spin with spin quantum number s and $\boldsymbol{\kappa} = \boldsymbol{k} - \boldsymbol{k}_0$. $\hbar\omega$ and $\hbar\boldsymbol{\kappa}$ are the energy- and momentum-transfers to the scattered neutrons respectively.

ZG take into account the correlation between different nuclear spins on the average. If one replaces $s_\nu \cdot s_{\nu'}$ in Eq. (1·2) by its average $\langle s_\nu \cdot s_{\nu'} \rangle$, this average, being independent of spin pairs, gives ZG's spin correlation term $Z(I)$:

$$Z(I) = \frac{\langle s_\nu \cdot s_{\nu'} \rangle}{s(s+1)} = \frac{I(I+1) - ns(s+1)}{s(s+1)n(n-1)}, \quad (\nu \neq \nu') \tag{1·3}$$

where n is the number of identical nuclei in a molecule and I the total spin quantum number. If the number of spin multiplets appearing in the intermediate states with the same energy is appropriately large, the above approximation seems to be valid. Otherwise it is open to question. We note here that the spacial part of the total state does correlate strongly with the spin part of it through statistics of nuclei. No careful study on the approximate nature of the ZG decoupling procedure has been done. It is the aim of this paper to elucidate this point with particular reference to methane.

In § 2 we give the symmetrized spin-rotational wave functions of a tetrahedral hydrogenic molecule whence we calculate in § 3 the matrix elements of transition between rotational levels. The spin-rotational part of the intermediate scattering function is treated in § 4 and the relation of our exact theory to ZG- and the uncorrelated approximations is described in § 5. The differential scattering cross section of methane gas is computed and compared with those in ZG- and uncorrelated approximations for several cases in § 6.

§ 2. Symmetrized spin-rotational wave functions

Throughout our study the electronic and vibrational states of the molecule are assumed to be in the ground state; an assumption relevant to the scattering of slow neutrons. We shall, for a moment, leave them out of our consideration.

Though the methane molecule is of T_d symmetry, it is sufficient to confine ourselves to T group. This is equivalent to the alternating group of four letters, i.e., the group of even permutations on them, which is relevant to the proper rotation. There are four irreducible representations A, F, E_1 and E_2 with respective dimension equal to $1, 3, 1$ and 1 in the considered group. The representations E_1 and E_2 appearing as a pair are the complex conjugate representation to each other.

The spin wave functions are shown in Table I, in agreement with Anderson and Ramsey's tabulation[10] except for E symmetry. As is shown in Table I, the total spin pertaining to the representation A, F and E are respectively $I = 2, 1$ and 0.

Table I. Symmetrized spin wave functions $\psi_s(\Gamma\sigma; IM)$ of the four proton system.

Γ	I	σ	M	$\psi_s\ (\Gamma\sigma; IM)$
A	2		2	$\alpha\alpha\alpha\alpha$
			1	$[\beta\alpha\alpha\alpha+\alpha\beta\alpha\alpha+\alpha\alpha\beta\alpha+\alpha\alpha\alpha\beta]/2$
			0	$[\alpha\alpha\beta\beta+\beta\beta\alpha\alpha+\alpha\beta\beta\alpha+\beta\alpha\alpha\beta+\alpha\beta\alpha\beta+\beta\alpha\beta\alpha]/\sqrt{6}$
			-1	$[\alpha\beta\beta\beta+\beta\alpha\beta\beta+\beta\beta\alpha\beta+\beta\beta\beta\alpha]/2$
			-2	$\beta\beta\beta\beta$
F	1	1	1	$[(\beta\alpha\alpha\alpha-\alpha\alpha\alpha\beta)-(\alpha\beta\alpha\alpha-\alpha\alpha\beta\alpha)]/2$
			0	$[\beta\alpha\beta\alpha-\alpha\beta\alpha\beta]/\sqrt{2}$
			-1	$[(\alpha\beta\beta\beta-\beta\beta\beta\alpha)-(\beta\alpha\beta\beta-\beta\beta\alpha\beta)]/2$
		2	1	$[(\alpha\beta\alpha\alpha+\alpha\alpha\beta\alpha)-(\beta\alpha\alpha\alpha+\alpha\alpha\alpha\beta)]/2$
			0	$[\alpha\beta\beta\alpha-\beta\alpha\alpha\beta]/\sqrt{2}$
			-1	$[(\beta\beta\beta\alpha+\alpha\beta\beta\beta)-(\beta\alpha\beta\beta+\beta\beta\alpha\beta)]/2$
		3	1	$[(\beta\alpha\alpha\alpha-\alpha\alpha\alpha\beta)+(\alpha\beta\alpha\alpha-\alpha\alpha\beta\alpha)]/2$
			0	$[\beta\beta\alpha\alpha-\alpha\alpha\beta\beta]/\sqrt{2}$
			-1	$[(\alpha\beta\beta\beta-\beta\beta\beta\alpha)+(\beta\alpha\beta\beta-\beta\beta\alpha\beta)]/2$
E_1	0		0	$[(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)+\varepsilon(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)+\varepsilon^2(\alpha\alpha\beta\beta+\beta\beta\alpha\alpha)]/\sqrt{6}$
E_2	0		0	$[(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)+\varepsilon^2(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)+\varepsilon(\alpha\alpha\beta\beta+\beta\beta\alpha\alpha)]/\sqrt{6}$

$\varepsilon = e^{i2\pi/3}$

Next, the construction of the *symmetrized rotational wave functions* of the tetrahedral molecule has been discussed by various authors.[11]~[13] These functions are written formally.

$$\psi_m^{(j)}(\Gamma\mu\sigma) = N^{-1/2} \sum_G a_{\sigma\tau}^{(\Gamma)*}(G)\widehat{G}\phi_{mk}^{(j)},\qquad (2\cdot1)$$

where $\widehat{G}$ is an element of our alternating group, representing the proper rotation, and N the normalization constant. We note here that μ on the left side of the above expression depends on k in the starting function $\phi_{mk}^{(j)}$, the wave function of spherical rotor, which is expressed in terms of the element of rotation matrix[14]

$$\phi_{mk}^{(j)}(\alpha\beta\gamma) = [(2j+1)/8\pi^2]^{1/2}\mathscr{D}_{mk}^{(j)}(\alpha\beta\gamma).\qquad (2\cdot2)$$

Here $(\alpha\beta\gamma)$ is a set of Euler angles of the body-fixed coordinates, $O\xi\eta\zeta$, relative to the space-coordinates system, where the coordinates system is taken as illustrated in Fig. 1. In Eq. $(2\cdot1)$ the coefficient $a_{\sigma\tau}^{(\Gamma)}(G)$ is an element of the representation matrix Γ, which is obtained by observing the transformation properties of symmetrized spin wave functions. The independent functions can be generated with a fixed τ. The results are as follows: For $\Gamma = A$,

$$\psi_m^{(j)}(A\mu) = (N_{A\mu}^{(j)})^{-1/2} \sum_n [\delta_{n\,2\mu} + (-1)^j\delta_{n-2\mu} + \{1+(-1)^n\}\{(-1)^\mu + i^n\}\varDelta_{n\,2\mu}^{(j)}]\phi_{mn}^{(j)},$$

$$N_{A\mu}^{(j)} = 6[1+(-1)^j\delta_{\mu\,0}+4(-1)^\mu\varDelta_{2\mu\,2\mu}^{(j)}],\qquad (2\cdot3)$$
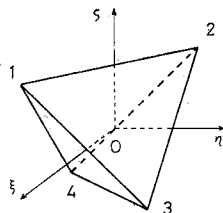
Fig. 1. Coordinates system $O\xi\eta\zeta$ fixed in the molecule.

where $N_{A\mu}^{(j)}$ is the normalization constant and

$$\Delta_{mm'}^{(j)} = \mathscr{D}_{mm'}^{(j)}(0, \pi/2, 0). \tag{2.4}$$

We note here that the suffix k in the starting function must be an even integer. Then we put $k=2\mu$. For $\Gamma = F$,

$$\psi_m^{(j)}(F\mu 1) = (N_{F\mu}^{(j)})^{-1/2}(-1)^\mu \sum_n [1-(-1)^n]\Delta_{n2\mu}^{(j)}\phi_{mn}^{(j)},$$

$$\psi_m^{(j)}(F\mu 2) = (N_{F\mu}^{(j)})^{-1/2} \sum_n i^n[1-(-1)^n]\Delta_{n2\mu}^{(j)}\phi_{mn}^{(j)},$$

$$\psi_m^{(j)}(F\mu 3) = (N_{F\mu}^{(j)})^{-1/2} \sum_n [\delta_{n2\mu}-(-1)^j\delta_{n-2\mu}]\phi_{mn}^{(j)},$$

$$N_{F\mu}^{(j)} = 2[1-(-1)^j\delta_{\mu 0}]. \tag{2.5}$$

We can easily show the orthogonality among $\psi_m^{(j)}(\Gamma\mu\sigma)$ with different μ. For $\Gamma = E$,

$$\psi_m^{(j)}(E_1\mu) = (N_{E\mu}^{(j)})^{-1/2}\sum_n [\delta_{n2\mu}+(-1)^j\delta_{n-2\mu}+\{1+(-1)^n\}\{\varepsilon(-1)^\mu+\varepsilon^2 i^n\}\Delta_{n2\mu}^{(j)}]\phi_{mn}^{(j)},$$

$$N_{E\mu}^{(j)} = 6[1+(-1)^j\delta_{\mu 0}-2(-1)^\mu\Delta_{2\mu 2\mu}^{(j)}]. \tag{2.6}$$

Here $\psi_m^{(j)}(E_2\mu)$ is given by Eq. (2.6) with replacement of $\varepsilon = e^{i2\pi/3}$ by $\varepsilon^* = e^{-i2\pi/3}$.

In the above functions, $\psi_m^{(j)}(\Gamma\mu\sigma)$ with negative μ differs only by a phase factor from that with positive μ, as is proved with the help of $\Delta_{mm'}^{(j)} = (-1)^{m-m'}\Delta_{-m-m'}^{(j)}$ and $\Delta_{mm'}^{(j)} = (-1)^{j-m}\Delta_{m-m'}^{(j)}$. Hence we take μ to be non-negative. The number of triplets F contained in the manifold with given j proves to be $j/2$ for even j and $(j+1)/2$ for odd j, owing to the mentioned orthogonality. The numbers of the other Γ contained in the same manifold are obtained from the group theoretical results,[15],[16] where one gets μ in the independent function $\psi_m^{(j)}(\Gamma\mu)$ as follows.

Γ \ j	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
A	0			1	0		0	1	0	1	0	1	0	1	0	1	
							1			2	1		1	2	1	2	(2.7)
													2			3	
E			0		0	1	0	1	0	1	0	1	0	1	0	1	
									1		1	2	1	2	1	2	
															2		

We note here that the symmetry A is splitted into A_1 and A_2 under the group T_d. The function (2·3) with even μ is of the A_1-symmetry while that with odd μ is of the other symmetry. The orthogonality between two functions with respective symmetries A_1 and A_2 can be easily seen from Eq. (2·3). The non-orthogonal functions appear first at $j=8$ for $\Gamma=E$ and at $j=12$ for $\Gamma=A$, where we take the well-known orthogonalization procedure.

Finally the *totally symmetric wave function* is written

$$\Psi(\Gamma\mu; jm; IM) = d_\Gamma^{-1/2} \sum_{\sigma=1}^{d_\Gamma} \psi_m^{(j)}(\Gamma\mu\sigma)\psi_s(\Gamma^*\sigma; IM), \qquad (2\cdot8)$$

where Γ^* is the complex conjugate representation to Γ and d_Γ the dimension of Γ.

§ 3. Matrix element

Before going into the intermediate scattering function, the matrix elements relevant to its evaluation will be given separately for the spin and rotational parts.

(a) *Spin part* Let $s_{q\nu}$ be the q-th component of the ν-th proton spin as defined by

$$s_{0\nu} = s_{z\nu}, \quad s_{\pm1\nu} = \mp 2^{-1/2}(s_{x\nu} \pm is_{y\nu}). \qquad (3\cdot1)$$

Let us now consider the following operator:

$$I_q^{(\tau)} = \sum_\nu c_{\nu\tau} s_{q\nu} \qquad (3\cdot2)$$

with $c_{\nu\tau}$ given by

τ \ ν	1	2	3	4
0	1	1	1	1
1	1	−1	1	−1
2	−1	1	1	−1
3	1	1	−1	−1

$$(3\cdot3)$$

which satisfies

$$\sum_\tau c_{\nu\tau} c_{\nu'\tau} = 4\delta_{\nu\nu'}, \quad \sum_\nu c_{\nu\tau} c_{\nu\tau'} = 4\delta_{\tau\tau'}. \qquad (3\cdot4)$$

We can show that $I_q^{(\tau)}$ with $q=0, \pm1$ constitute a set of tensor operators for each τ. According to the Wigner-Eckart theorem we have

$$\langle \Gamma'\sigma'; I'M'|I_q^{(\tau)}|\Gamma\sigma; IM\rangle$$

$$= (-1)^{I'-M'}\begin{pmatrix} I' & 1 & I \\ -M' & q & M \end{pmatrix}\langle \Gamma'\sigma'; I'\|I^{(\tau)}\|\Gamma\sigma; I\rangle \qquad (3\cdot5)$$

in terms of the Wigner $3j$-symbol, where the double-bar matrix element can be obtained from evaluation of a particular matrix element. It is easily proved that $I_q^{(\tau)}$ with $\tau=0$ is of A-symmetry and that $I_q^{(\tau)}$ with $\tau=1,2$ and 3 constitute the bases of F-symmetry, $(F1)$, $(F2)$ and $(F3)$. Thus we replace τ by $(\Gamma\sigma)$.

With the above labeling the non-vanishing double-bar matrix elements in Eq. $(3\cdot5)$ are given by

$$\langle\Gamma'\sigma';\ \Gamma'\|I^{(A)}\|\Gamma\sigma;\ I\rangle=[I(I+1)(2I+1)]^{1/2}\delta_{\Gamma\Gamma'}\delta_{\sigma\sigma'}\delta_{II'},$$
$$\langle F\sigma';\ 1\|I^{(F\sigma'')}\|A;\ 2\rangle=\sqrt{10}\delta_{\sigma'\sigma''},$$
$$\langle F\sigma';\ 1\|I^{(F\sigma'')}\|F\sigma;\ 1\rangle=\sqrt{6}e^2_{\sigma'\sigma''\sigma},$$
$$\langle F\sigma';\ 1\|I^{(F\sigma'')}\|E_{\iota};\ 0\rangle=-2\varepsilon^{\iota\sigma'}\delta_{\sigma'\sigma''},$$

(3·6)

where $e_{\sigma'\sigma''\sigma}$ is the usual antisymmetric unit tensor with rank 3[*] and $\varepsilon^{\iota\sigma'}=e^{i2\pi\iota\sigma'/3}$.

(b) *Rotational part* We describe here the matrix element of a tensor operator $T_m^{(l)}(\Gamma\mu\sigma)$ defined by

$$T_m^{(l)}(\Gamma\mu\sigma)=[8\pi^2/(2l+1)]^{1/2}\psi_m^{(l)}(\Gamma\mu\sigma),$$

(3·7)

where $\psi_m^{(l)}(\Gamma\mu\sigma)$ is the symmetrized rotational wave function given in §2. By the same procedure as Eq. $(3\cdot5)$ was obtained, we have[14]

$$\langle\Gamma_1\mu_1\sigma_1;\ j_1m_1|\,T_m^{(l)}(\Gamma\mu\sigma)\,|\Gamma_2\mu_2\sigma_2;\ j_2m_2\rangle$$
$$=(-1)^{j_1-m_1}\begin{pmatrix}j_1 & l & j_2\\ -m_1 & m & m_2\end{pmatrix}\langle\Gamma_1\mu_1\sigma_1;\ j_1\|T^{(l)}(\Gamma\mu\sigma)\|\Gamma_2\mu_2\sigma_2;\ j_2\rangle.$$ (3·8)

The above double-bar matrix elements are calculated as follows:

$$\langle F\mu_1\sigma_1;\ j_1\|T^{(l)}(F\mu\sigma)\|F\mu_2\sigma_2;\ j_2\rangle=(e_{\sigma_1\sigma\sigma_2})^{\mu_1+\mu+\mu_2+1}p,$$

(3·9a)

$$p=-8[(2j_1+1)(2j_2+1)]^{1/2}(N_{F\mu_1}^{(j_1)}N_{F\mu}^{(l)}N_{F\mu_2}^{(j_2)})^{-1/2}$$
$$\times(-1)^{j_1+\mu_1}\sum_{\lambda:\,\mathrm{odd}}i^\lambda\varDelta_{2\mu_1 2\mu_2+\lambda}^{(j_1)}\varDelta_{2\mu\,\lambda}^{(l)}\begin{pmatrix}j_1 & l & j_2\\ -2\mu_2-\lambda & \lambda & 2\mu_2\end{pmatrix};$$ (3·9b)

$$\langle F\mu_1\sigma_1;\ j_1\|T^{(l)}(F\mu\sigma)\|E_{\iota}\mu_2;\ j_2\rangle=\varepsilon^{\iota\sigma}\delta_{\sigma_1\sigma}q,$$

(3·10a)

$$q=2[(2j_1+1)(2j_2+1)]^{1/2}(N_{F\mu_1}^{(j_1)}N_{F\mu}^{(l)}N_{E\mu_2}^{(j_2)})^{-1/2}$$
$$\times(-1)^{j_1}\sum_{\lambda=\pm1}\{\delta_{\lambda1}-(-1)^l\delta_{\lambda-1}\}\left[\begin{pmatrix}j_1 & l & j_2\\ -2\mu_1 & 2\lambda\mu & 2\mu_2\end{pmatrix}+(-1)^{j_2}\begin{pmatrix}j_1 & l & j_2\\ -2\mu_1 & 2\lambda\mu & -2\mu_2\end{pmatrix}\right.$$
$$\left.+2\{\varepsilon(-1)^{\mu_2}+\varepsilon^2(-1)^{\mu+\mu_1}\}\varDelta_{2\mu_2 2\mu_1-2\lambda\mu}^{(j_2)}\begin{pmatrix}j_1 & l & j_2\\ -2\mu_1 & 2\lambda\mu & 2\mu_1-2\lambda\mu\end{pmatrix}\right],$$ (3·10b)

$$\langle F\mu_1\sigma_1;\ j_1\|T^{(l)}(F\mu\sigma)\|A\mu_2;\ j_2\rangle=\delta_{\sigma_1\sigma}q'$$

(3·11)

where q' is given by q of Eq. $(3\cdot10\text{b})$ with $N_{E\mu_2}^{(j_2)}$ and ε replaced by $N_{A\mu_2}^{(j_2)}$ and 1 respectively.

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[*] $e_{123}=e_{231}=e_{312}=1$, $e_{132}=e_{321}=e_{213}=-1$ and otherwise zero.

For $\Gamma = A$, $\langle \Gamma_1 \mu_1 \sigma_1; j_1 \| T^{(l)} (A\mu) \| \Gamma_2 \mu_2 \sigma_2; j_2 \rangle$ vanishes unless $\Gamma_1 = \Gamma_2$ and $\sigma_1 = \sigma_2$, whose expression is rather lengthy and may be omitted here.

§ 4. Intermediate scattering function

We assume that the intermediate scattering function $\chi^{\nu\nu'}$ defined by Eq. (1·2) can be separated into the translational, vibrational and spin-rotational parts:

$$\chi^{\nu\nu'} = \chi_{\text{tr}}^{\nu\nu'} \chi_{\text{vib}}^{\nu\nu'} \chi_{\text{spin-rot}}^{\nu\nu'} , \qquad (4\cdot1)$$

where $\chi_{\text{tr}}^{\nu\nu'}$ is well known[1] and $\chi_{\text{vib}}^{\nu\nu'}$ reduces to the Debye-Waller factor $\exp(-\kappa^2 \gamma_{\nu\nu'})$ for the cold neutron scattering.[3] The $\gamma_{\nu\nu'}$'s are the same for all pairs of protons including the $\nu = \nu'$ case,[3] which is denoted by γ_p.

Now we look into $\chi_{\text{spin-rot}}^{\nu\nu'}$. Considering $\chi_{\text{tr}}^{\nu\nu'}$ and $\chi_{\text{vib}}^{\nu\nu'}$ to be independent of ν and ν', we have

$$\sum_{\nu\nu'} \chi_{\text{spin-rot}}^{\nu\nu'} = \sum_{\nu\nu'} \langle \exp(i\boldsymbol{\kappa} \cdot \boldsymbol{b}_\nu(t)) \boldsymbol{s}_\nu \cdot \boldsymbol{s}_{\nu'} \exp(-i\boldsymbol{\kappa} \cdot \boldsymbol{b}_{\nu'}(0)) \rangle . \qquad (4\cdot2)$$

If we expand $\exp(i\boldsymbol{\kappa} \cdot \boldsymbol{b}_\nu)$ in terms of the spherical Bessel function j_l and the Legendre polynomial with reference to the body-fixed system, Eq. (4·2) becomes

$$\sum_{\nu\nu'} \chi_{\text{spin-rot}}^{\nu\nu'} = \sum_{l=0}^{\infty} (2l+1) \{j_l(\kappa b)\}^2 f_l(t), \qquad (4\cdot3)$$

$$f_l(t) = \sum_{qm} \langle G_{qm}^{(l)}(t) G_{qm}^{(l)'}(0) \rangle . \qquad (4\cdot4)$$

Here $\boldsymbol{b}_\nu$ is the position vector of the ν-th proton relative to the mass center, whose magnitude is denoted by b. $G_{qm}^{(l)}$ is given by

$$G_{qm}^{(l)} = [4\pi/(2l+1)]^{1/2} \sum_{m'} \mathscr{D}_{mm'}^{(l)}(\alpha\beta\gamma) \sum_\nu Y_{l-m'}^*(\theta_\nu, \varphi_\nu) s_{q\nu}, \qquad (4\cdot5)$$

where (θ_ν, ϕ_ν) are the polar angle coordinates of the ν-th proton with respect to the coordinates system $O\xi\eta\zeta$ illustrated in Fig. 1 and $Y_{lm}(\theta, \phi)$ a spherical harmonic function.

Now $G_{qm}^{(l)}$ must be invariant under even permutation of protons. The required form is

$$G_{qm}^{(l)} = \sum_{\Gamma\sigma} I_q^{(\Gamma\sigma)} g_m^{(l)}(\Gamma\sigma), \qquad (4\cdot6)$$

$$g_m^{(l)}(\Gamma\sigma) = \sum_\mu b_\mu^{(l)}(\Gamma) T_m^{(l)}(\Gamma\mu\sigma), \qquad (4\cdot7)$$

where $T_m^{(l)}(\Gamma\mu\sigma)$ is defined by Eq. (3·7) and the expansion coefficients $b_\mu^{(l)}(\Gamma)$ are tabulated in Table II up to $l=6$. We note that the terms with $\Gamma = E$ do not appear. We also note that $b_\mu^{(l)}(\Gamma)$ is independent of σ because of the invariance property of $G_{qm}^{(l)}$ mentioned above.

If we use Eqs. (3·5) and (3·8), the matrix elements of $G_{qm}^{(l)}$ with respect to the totally symmetric wave function (2·8) is written

Table II. Expansion coefficients $b_\mu^{(l)}(\Gamma)$.

l	$b_\mu^{(l)}(A)$	$b_\mu^{(l)}(F)$
0	$\delta_{\mu 0}$	0
1	0	$\dfrac{1}{\sqrt{3}}\delta_{\mu 0}$
2	0	$-\dfrac{i}{\sqrt{3}}\delta_{\mu 1}$
3	$-i\dfrac{\sqrt{5}}{3}\delta_{\mu 1}$	$-\dfrac{2}{3\sqrt{3}}\delta_{\mu 0}$
4	$-\dfrac{\sqrt{7}}{3\sqrt{3}}\delta_{\mu 0}$	$-i\dfrac{2\sqrt{5}}{9}\delta_{\mu 1}$
5	0	$-\dfrac{1}{6\sqrt{3}}\delta_{\mu 0}-\dfrac{\sqrt{35}}{6\sqrt{3}}\delta_{\mu 2}$
6	$\dfrac{4\sqrt{2}}{9}\delta_{\mu 0}$	$i\dfrac{\sqrt{35}}{6\sqrt{6}}\delta_{\mu 1}+i\dfrac{\sqrt{77}}{18\sqrt{6}}\delta_{\mu 3}$

$$\langle \Gamma_1\mu_1;\ j_1m_1;\ I_1M_1|G_{qm}^{(l)}|\Gamma_2\mu_2;\ j_2m_2;\ I_2M_2\rangle$$

$$= (-1)^{j_1+I_1-m_1-M_1}\begin{pmatrix} I_1 & 1 & I_2 \\ -M_1 & q & M_2 \end{pmatrix}\begin{pmatrix} j_1 & l & j_2 \\ -m_1 & m & m_2 \end{pmatrix}$$

$$\times \langle \Gamma_1\mu_1;\ j_1I_1\|G^{(l)}\|\Gamma_2\mu_2;\ j_2I_2\rangle, \tag{4.8}$$

where

$$\langle \Gamma_1\mu_1;\ j_1I_1\|G^{(l)}\|\Gamma_2\mu_2;\ j_2I_2\rangle$$

$$= (d_{\Gamma_1}d_{\Gamma_2})^{-1/2}\sum_{\sigma_1\sigma_2}\sum_{\Gamma\sigma}\langle \Gamma_1\sigma_1;\ I_{\Gamma_1}\|I^{(\Gamma\sigma)}\|\Gamma_2\sigma_2;\ I_{\Gamma_2}\rangle$$

$$\times \langle \Gamma_1\mu_1\sigma_1;\ j_1\|g^{(l)}(\Gamma\sigma)\|\Gamma_2\mu_2\sigma_2;\ j_2\rangle \tag{4.9}$$

with

$$\langle \Gamma_1\mu_1\sigma_1;\ j_1\|g^{(l)}(\Gamma\sigma)\|\Gamma_2\mu_2\sigma_2;\ j_2\rangle$$

$$= \sum_\mu b_\mu^{(l)}(\Gamma)\langle \Gamma_1\mu_1\sigma_1;\ j_1\|T^{(l)}(\Gamma\mu\sigma)\|\Gamma_2\mu_2\sigma_2;\ j_2\rangle. \tag{4.10}$$

Substituting Eq. (4·8) into Eq. (4·4) and using the well-known orthogonality relation of $3j$-symbol,[14] we have

$$f_l(t) = Z^{-1}\sum_{j_1j_2}f_l(j_1;\ j_2)\exp[-\beta\varepsilon_{j_1}+i(\varepsilon_{j_1}-\varepsilon_{j_2})t/\hbar], \tag{4.11}$$

$$f_l(j_1;\ j_2) = \sum_{\Gamma_1\mu_1}\sum_{\Gamma_2\mu_2}|\langle \Gamma_1\mu_1;\ j_1I_{\Gamma_1}\|G^{(l)}\|\Gamma_2\mu_2;\ j_2I_{\Gamma_2}\rangle|^2, \tag{4.12}$$

where $\beta=1/k_BT$, $\varepsilon_j=Bj(j+1)$ with rotational constant B and Z is the partition function

$$Z = \sum_{j\Gamma}(2j+1)(2I_\Gamma+1)n_\Gamma^{(j)}\exp(-\beta\varepsilon_j). \tag{4.13}$$

Here $I_\Gamma=2, 1$ and 0 respectively for $\Gamma=A, F$ and E, and $n_\Gamma^{(j)}$ is the number of

representation Γ contained in the manifold with the same rotational quantum number j.

If we use Eq. (4·6) with Eqs. (3·6), (3·9a), (3·10a) and (3·11), Eq. (4·12) is written as

$$f_i(j_1;\ j_2) = \sum_{\Gamma_1\mu_1} \sum_{\Gamma_2\mu_2} \sum_{\Gamma\Gamma'} \Omega_{\Gamma_1\Gamma_2}(\Gamma,\Gamma')$$
$$\times H^{(\Gamma)}(\Gamma_1\mu_1 j_1;\ \Gamma_2\mu_2 j_2) H^{(\Gamma')}(\Gamma_1\mu_1 j_1;\ \Gamma_2\mu_2 j_2)^*, \qquad (4\cdot14)$$

$$H^{(\Gamma)}(\Gamma_1\mu_1 j_1;\ \Gamma_2\mu_2 j_2) = (d_{\Gamma_1} d_{\Gamma_2})^{-1/2} \sum_{\sigma_1\sigma\sigma_2}$$
$$\times \langle \Gamma_1\mu_1\sigma_1;\ j_1 \| h^{(l)}(\Gamma\sigma) \| \Gamma_2\mu_2\sigma_2;\ j_2 \rangle. \qquad (4\cdot14a)$$

In the above expression, the double-bar matrix element of $h^{(l)}(\Gamma\sigma)$ is to be identified with that of $g^{(l)}(\Gamma\sigma)$ unless $\Gamma_1=\Gamma=F$ and $\Gamma_2=E$ or $\Gamma_1=E$ and $\Gamma=\Gamma_2 =F$. If $\Gamma_1=\Gamma=F$, $\Gamma_2=E$,

$$\langle F\mu_1\sigma_1;\ j_1 \| h^{(l)}(F\sigma) \| E_{\mu_2};\ j_2 \rangle = \varepsilon^{-i\sigma}\langle F\mu_1\sigma_1;\ j_1 \| g^{(l)}(F\sigma) \| E_{\mu_2};\ j_2 \rangle. \qquad (4\cdot15)$$

The coefficients $\Omega_{\Gamma_1\Gamma_2}(\Gamma,\Gamma')$ are given on the first line of Table III.

Table III. Non-vanishing values for the coefficients $\Omega_{\Gamma_1\Gamma_2}(\Gamma,\Gamma')$.

	$\Omega_{rr}(A,A)$	Ω_{FA} (F,F)	Ω_{AF} (F,F)	Ω_{FE} (F,F)	Ω_{EF} (F,F)	Ω_{FF} (F,F)	Ω_{FF} (A,F)	Ω_{FF} (F,A)
Exact	$I_r(I_r+1)(2I_r+1)$	10	10	4	4	6	6	6
ZG	$I_r(I_r+1)(2I_r+1)$	10/3	10	10/3	4	5	0	0
Uncorrel.	$3d_r$	3	3	3	3	9/2	0	0

We finally introduce $\tilde{h}^{(l)}(\Gamma\sigma)$ by the following: The double-bar matrix element of $\tilde{h}^{(l)}(\Gamma\sigma)$ is identical to that of $h^{(l)}(\Gamma\sigma)$ unless $\Gamma_1=\Gamma=\Gamma_2=F$. If $\Gamma_1=\Gamma=\Gamma_2=F$,

$$\langle F\mu_1\sigma_1;\ j_1 \| \tilde{h}^{(l)}(F\sigma) \| F\mu_2\sigma_2;\ j_2 \rangle$$
$$= e^2_{\sigma_1\sigma\sigma_2} \sum_\mu b_\mu{}^{(l)}(F)\langle F\mu_1;\ j_1 \| T^{(l)}(F\mu 2) \| F\mu_2 3;\ j_1 \rangle. \qquad (4\cdot16)$$

The above quantity, $\tilde{h}^{(l)}(\Gamma\sigma)$, will be used in §5.

§5. ZG- and uncorrelated approximations

(a) *ZG-approximation* According to ZG, the intermediate scattering function is written

$$\sum_{\nu\nu'} \chi^{\nu\nu'}_{\text{spin-rot}} = s(s+1) \sum_\Gamma \{ Z(I_\Gamma) \sum_{\nu\nu'} \langle f_{\nu\nu'}(t) \rangle_\Gamma + [1-Z(I_\Gamma)] \sum_\nu \langle f_{\nu\nu}(t) \rangle_\Gamma \}, \qquad (5\cdot1)$$

where $f_{\nu\nu'}(t) = \exp[i\boldsymbol{\kappa}\cdot\boldsymbol{b}_\nu(t)]\exp[-i\boldsymbol{\kappa}\cdot\boldsymbol{b}_{\nu'}(0)]$ and $Z(I)$ is the ZG correlation factor defined by Eq. (1·3). And $\langle\ \rangle_\Gamma$ means a contribution from the states with representation Γ to the average:

$$\langle f\rangle_r = Z^{-1}\sum_\alpha \langle \Gamma I_r\alpha|f|\Gamma I_r\alpha\rangle e^{-\beta\varepsilon_\alpha}\,, \tag{5.2}$$

where α represents a set of quantum numbers $(\mu; j, m; M)$. By the same procedure as was taken in the preceding section, Eq. (5·1) is written in the form (4·3), where $f_l(t)$ is now given by

$$f_l(t) = s(s+1)\sum_{m\Gamma}\Big\{Z(I_\Gamma)\sum_{\nu\nu'}\langle g^{(l)}_{m\nu}(t)g^{(l)*}_{m\nu'}(0)\rangle_r$$

$$+\,[1-Z(I_\Gamma)]\sum_{\nu}\langle g^{(l)}_{m\nu}(t)g^{(l)*}_{m\nu}(0)\rangle_r\Big\} \tag{5.3}$$

with

$$g^{(l)}_{m\nu} = [4\pi/(2l+1)]^{1/2}\sum_{m'}\mathscr{D}^{(l)}_{mm'}(\alpha\beta\gamma)\,Y^*_{l-m'}(\theta_\nu,\phi_\nu). \tag{5.4}$$

Comparison of Eq. (5·4) with Eq. (4·5) leads to

$$G^{(l)}_{qm} = \sum_\nu g^{(l)}_{m\nu}s_{q\nu}\,. \tag{5.5}$$

Substituting Eq. (3·2) into Eq. (4·6) and comparing the resulting expression with Eq. (5·5), we have

$$g^{(l)}_{m\nu} = \sum_{\Gamma\sigma} c_{\nu,\Gamma\sigma}\,g^{(l)}_{m,\Gamma\sigma}\,, \tag{5.6}$$

where a suffix τ in Eq. (3·2) is replaced by $(\Gamma\sigma)$ and $g^{(l)}_{m,\Gamma\sigma}\equiv g_m^{(l)}(\Gamma\sigma)$.

If we substitute the above expression into Eq. (5·3) and use Eqs. (3·3) and (3·4), $f_l(t)$ becomes

$$f_l(t) = 4s(s+1)\sum_{m\Gamma}\Big\{4Z(I_\Gamma)\langle g^{(l)}_{m,A}(t)g^{(l)*}_{m,A}(0)\rangle_r$$

$$+\,[1-Z(I_\Gamma)]\sum_{\Gamma'\sigma'}\langle g^{(l)}_{m,\Gamma'\sigma'}(t)g^{(l)*}_{m,\Gamma'\sigma'}(0)\rangle_r\Big\}, \tag{5.7}$$

where the sum inside the brace runs over $\Gamma'=A$ and F.

In accordance with SV's treatment, we replace the above average by the average over the *totally symmetric states*, while the intermediate states are taken to be the *symmetrized rotational states*. The resulting expression can be written in the form (4·11), where $f_l(j_1; j_2)$ is given by Eq. (4·14) with $h^{(l)}(\Gamma\sigma)=\tilde{h}^{(l)}(\Gamma\sigma)$ and with different coefficients $\Omega_{\Gamma_1\Gamma_2}(\Gamma,\Gamma')$ shown on the second line of Table III. The approximation $h^{(l)}(\Gamma\sigma)=\tilde{h}^{(l)}(\Gamma\sigma)$ violates the selection rule for transitions $\Gamma_1=\Gamma=\Gamma_2=F$, which states that $H^{(F)}(F\mu_1 j_1; F\mu_2 j_2)$ should vanish identically if $\mu_1+\mu+\mu_2$ is an even integer according to Eq. (3·9a).

As is seen in Table III, the microscopic reversibility breaks down in ZG's approximation. Therefore the condition of detailed balance cannot be valid in this approximation. In Table IV, we explicitly compare the exact values of $|\langle\Gamma_1\mu_1; j_1 I_1\|G^{(l)}\|\Gamma_2\mu_2; j_2 I_2\rangle|^2$ with those of SV, which is based on the ZG approximation, for the particular case $l=1$.

(b) *Uncorrelated approximation* In this approximation, we have

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Table IV. Comparison of the exact values of $|\langle\Gamma_1\mu_1;j_1I_1\|G^{(1)}\|\Gamma_2\mu_2;j_2I_2\rangle|^2$ with those based on the ZG approximation. In the second column, the states are designated by $(\Gamma\mu)$. A, E and F in the third column refers to the initial state.

$j_1\rightarrow j_2$	Exact			ZG	
0→1	$(A0)\rightarrow(F0)$	10		A	10
1→0	$(F0)\rightarrow(A0)$	10		F	10/3
1	$(F0)\rightarrow(F0)$	0		F	10
2	$(F0)\rightarrow(E0)$	8 $\big\}$20		F	50/3
	$(F1)$	12			
2→1	$(F1)\rightarrow(F0)$	12		F	10
	$(E0)\rightarrow(F0)$	8		E	8
2	$(F1)\rightarrow(F1)$	0 $\big\}$40/3		F	50/3
	$(E0)$	40/3			
	$(E0)\rightarrow(F1)$	40/3		E	40/3
3	$(F1)\rightarrow(A1)$	50/3	74/3	F	70/3
	$(F0)$	8			
	$(F1)$	0			
	$(E0)\rightarrow(F0)$	12	56/3	E	56/3
	$(F1)$	20/3			

$$\sum_{\nu\nu'}\chi^{\nu\nu'}_{\text{spin-rot}}=s(s+1)\sum_\nu\langle f_{\nu\nu}(t)\rangle, \qquad (5\cdot8)$$

in place of Eq. (5·1), where the average is to be taken over the *unsymmetrized rotational states*. Now the symmetrized- and unsymmetrized-rotational states are transformed to each other through a unitary transformation. Owing to the invariance of diagonal sum in the unitary transformation, the above expression leads to Eq. (5·1) without the ZG factor $Z(I_r)$, where $\langle\ \rangle_r$ is to be regarded as a contribution from the *symmetrized rotational states* with representation Γ to the average.

By the same procedure as was taken before, $f_i(t)$ in the uncorrelated approximation is written in the form (5·7) without the ZG factor, where the average is to be taken over the *symmetrized rotational states*. Thus $f_i(t)$ in the approximation concerned can be written in the form (4·11), in which $f_i(j_1;j_2)$ is given by Eq. (4·14) with $h^{(l)}(\Gamma\sigma)=\tilde{h}^{(l)}(\Gamma\sigma)$ and with different coefficients $\Omega_{\Gamma_1\Gamma_2}(\Gamma,\Gamma')$ shown on the third line of Table III. However, one should note that the partition function Z' in the considered approximation is to be given by

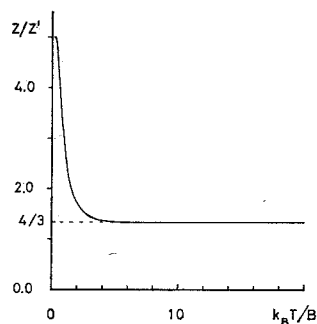$$Z'=\sum_j (2j+1)^2\exp(-\beta\varepsilon_j) \qquad (5\cdot9)$$

Fig. 2. Z/Z' versus k_BT/B (B =7.545K).

in place of Eq. (4·13): It is more relevant to compare $\Omega_{r_1 r_2}(\Gamma, \Gamma') Z/Z'$ with $\Omega_{r_1 r_2}(\Gamma, \Gamma')$ in the other theories. In Fig. 2, we plot Z/Z' as a function of temperature. One should also note that the condition of detailed balance is valid in the uncorrelated approximation.

§ 6. Differential scattering cross section

The incoherent part of the partial differential cross section is written

$$(d^2\sigma/d\Omega d\omega)_{\text{incoh}} = (2\pi)^{-1}(k/k_0)\,[C^2/s(s+1)]\exp(-\gamma_p\kappa^2)$$

$$\times (2\pi M\beta^2/\kappa)^{1/2}\sum_{l=0}^{\infty}(2l+1)\{j_l(\kappa b)\}^2 Z^{-1}\sum_{j_1 j_2}f(j_1;\,j_2)\exp(-\beta\varepsilon_{j_1})$$

$$\times \exp\left[-\{\hbar\omega+(\hbar^2\kappa^2/2M)+\varepsilon_{j_1}-\varepsilon_{j_2}\}^2 M\beta/(2\hbar^2\kappa^2)\right], \qquad (6\cdot1)$$

which is computed for methane gas for the following three cases.

The first case is the one taken up by SV,[9] i.e., the scattering of 25 meV neutrons with scattering angle 10° by a hypothetical methane gas at 10 K. The results are shown in Fig. 3, in which the results based on ZG's formula and those on the uncorrelated theory of Griffing[5] are also shown. Notice a considerable deviation of ZG spectra from the exact ones at the side of high energy; a result due to failure of the condition of detailed balance.

Secondly the computations are done for the case when the incident neutron energy is 4.6 meV with scattering angle 20° at temperature 293 K, which corresponds to one of Webb's experimental conditions.[17]
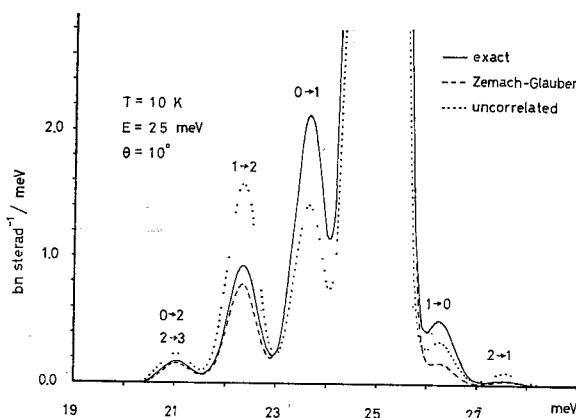

Fig. 3. Partial differential incoherent scattering cross section of a hypothetical methane gas at 10 K with the incident neutron energy 25 meV and the scattering angle 10°.

The resulting inelastic spectra are shown in Fig. 4, where contributions to the total spectra from the incoherent scattering with given l and those from the coherent scattering are separately shown in the same figure. In the present result the terms up to $j_1, j_2 = 15$ have been taken into account. The corresponding result in the ZG approximation is almost completely in agreement with the present result. As was mentioned by SV,[9] the spin correlation effect is negligibly small at high temperature. This is manifested by comparing the above result with the exact one based on the uncorrelated assumption,[7] which is given also in Fig. 4.
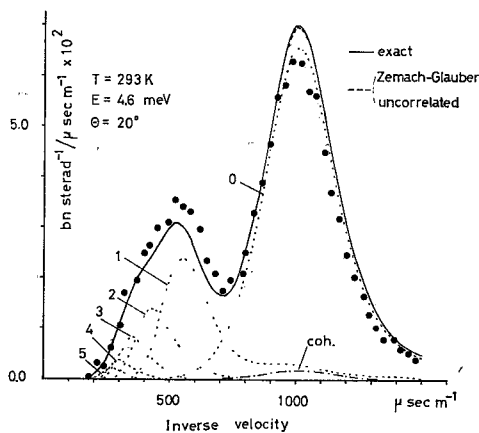
Fig. 4

Fig. 5

Fig. 4. Partial differential scattering cross section of methane gas at 293K with the incident neutron energy 4.6meV and the scattering angle 20°. The contributions to the total spectra from the incoherent scattering with given l and those from the coherent scattering are designated respectively by dotted and dot-broken lines.
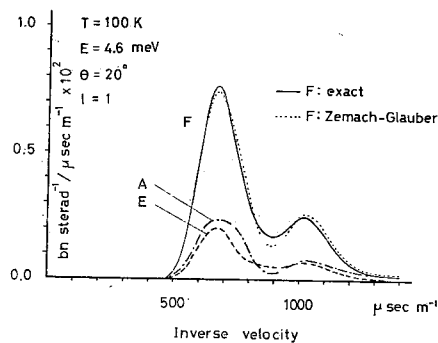
Fig. 5. Scattering spectra with $l=1$ at 100K with the incident energy 4.6meV and the scattering angle 20°. A, F and E represent symmetries of the initial states of transitions.

The third case is the one with the same incident energy and scattering angle as in the second case but at the lower temperature 100 K. For this case the total spectra come out almost from $l=0$, 1 and 2 terms. The scattering spectra for $l=1$ are compared with those based on the ZG approximation in Fig. 5, where A, F and E refer to symmetries of the initial states of transitions. For A and E symmetries the ZG approximation gives a result identical to the exact one, while a small but appreciable deviation occurs for the transitions from F-states.

We may conclude that the ZG approximation becomes worse at lower temperature. The deviation comes from the transitions related to F-states. This approximation may be serious in applying it to the scattering by molecules in condensed states at low temperature, which may be subjected to the crystalline and/or molecular fields due to surrounding molecules.[18],[19]

We finally compare our theoretical results with Webb's measurements[17] as shown in Fig. 4.[*] In this figure, we observe an appreciable difference to exist between the theoretical and experimental ones. There may be two possible reasons for the mentioned deviation. First, the effect of multiple scattering might

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[*] In Fig. 1 of Ref. 17), which has also been reproduced in the standard text,[22] the curve related to SV's approximation deviates appreciably from the measured data at the side of high energy transfer, in contradistinction with our corresponding one shown in Fig. 4. The discrepancy is supposed to come from an insufficient account of the contributions from higher values of l and/or j_1 and j_2. We note that SV's result has proved to be almost identical with the one in the uncorrelated approximation, which must approach Krieger and Nelkin's result at the side of high energy transfer as has been proved in the previous paper.[7]

still be effective, though Webb's sample was so thin.[20] Secondly, the C-H distance in a molecule is not perfectly rigid due to the zero-point motion of atoms. This effect has partly been taken into account in the form of the Debye-Waller factor. However, the most accurate theoretical calculation[21] shows that the mean value of the proton distance, $\langle r \rangle$, in hydrogen molecule is about 2% larger than the same distance estimated from another average $\langle r^{-2} \rangle$. The difference may be more considerable in methane. If it is the case, $\{j_l(\kappa b)\}^2$ with higher l will be more effective in comparison with the rigid-molecule approximation. A preliminary calculation shows that the above effect is in the right direction, though an assumed C-H distance larger than its current value by 5% is not sufficient to get a satisfactory agreement.

Acknowledgements

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