as the expectation value of the exact Hamiltonian with the wave function constructed from the approximate exchange potential. Examples of both types of computation exist. Tong and Sham[9] followed the first procedure of using Eq. (2), whereas Cowan *et al.*[10] followed the second procedure. For example, Tong and Sham's value for the total energy of Ar is -1049.027 Ry, whereas the value given by Cowan *et al.* is -1053.569 Ry, which is closer to the Hartree-Fock value of -1053.613 Ry. The second procedure gives a better value for the total energy since it amounts to using the exact expression for $E_x[n]$ even though the wave function is determined by using the exchange potential derived from an approximate expression for $E_x[n]$. It is precisely this inconsistency in the use of approximations which spoils the virial theorem.

---

[*] Supported in part by the National Science Foundation, Grant No. GP-14912.

[1] M. Berrondo and O. Goscinski, Phys. Rev. 184, 10 (1969).

[2] M. Ross, Phys. Rev. 179, 612 (1969).

[3] J. C. Slater, Phys. Rev. 81, 385 (1951).

[4] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[5] R. Gaspar, Acta Phys. Hung. 3, 263 (1954).

[6] P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

[7] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[8] W. E. Rudge, Phys. Rev. 181, 1033 (1969).

[9] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

[10] R. D. Cowan, A. Larson, D. Liberman, J. B. Mann, and J. Waber, Phys. Rev. 144, 5 (1966).

PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Rotational Correlation Functions and Neutron Scattering by Symmetric Molecules*

Ashok K. Agrawal*
Argonne National Laboratory, Argonne, Illinois 60439

and

Sidney Yip[†]
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 October 1969)

Classical rotational correlation functions for symmetric molecules are derived from quantum-mechanical results in neutron scattering. The analysis differs from an earlier calculation in that all values of the projection quantum number are considered. The results agree with those obtained by St. Pierre and Steele using classical statistical mechanics. Numerical results for ammonia and water are presented.

Recently, we discussed a method of studying slow-neutron scattering by molecular gases in terms of classical rotational correlation functions $F_l(t)$.[1] It was later pointed out by St. Pierre and Steele[2] that the symmetric rotor expression given in this work is not generally valid because the analysis considered only small values of the projection quantum number K. In this paper, we rederive $F_1(t)$ and $F_2(t)$ for symmetric molecules and obtain results which agree with those obtained by St. Pierre and Steele, who used a different approach. We also present numerical results for ammonia gas and water vapor which are in satisfactory agreement with experiment.

In dealing with neutron scattering from hydrogenous systems, the intermediate scattering function of a rigid rotor is[1]

$$\chi_r(\vec{\kappa}, t) = \langle e^{i\vec{\kappa}\cdot\vec{b}(t)}\, e^{-i\vec{\kappa}\cdot\vec{b}(0)}\rangle , \tag{1}$$

where $\vec{b}(t)$ is the position vector of the rotor at time t, $\vec{\kappa}$ is the momentum transfer variable, and $\langle\cdots\rangle$ denotes a quantum-mechanical thermal average. Evaluation of Eq. (1) proceeds from the expansion

$$\chi_\gamma(\kappa,t)=\sum_{l=0}^{\infty}(2l+1)j_l^2(\kappa b)f_l(t)\,, \tag{2}$$

where $j_l(x)$ is the lth-order spherical Bessel function of argument x. For symmetric rotors, quantum-mechanical calculations give[3,4]

$$f_l(t)=\sum_{JK}(2J+1)P_{JK}(T)\sum_{J'K'}{}' e^{i(E_{JK}-E_{J'K'})t}\frac{(l-|K-K'|)!}{(l+|K-K'|)!}\left|P_l^{|K-K'|}(\cos\phi)\right|^2\begin{bmatrix} J & l & J' \\ K & K'-K & K'\end{bmatrix}^2\,, \tag{3}$$

where $P_{JK}(T)=e^{-E_{JK}/T}\Big/\sum_{J'K'}(2J'+1)e^{-E_{J'K'}/T}$ and $\begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3\end{bmatrix}$ (4)

denote the usual Clebsch-Gordan coefficient.[5] The rotor energies are denoted by E_{JK}, and ϕ is the angle between $\vec{b}(t)$ and the symmetry axis.

The method of obtaining classical correlation functions from Eq. (3) has been discussed previously.[1,6] It was observed that one can make use of the condition $1/2I \ll T$ and consider the major contribution in Eq. (3) to come from large J values. The classical functions are then given by the real part of $f_l(t)$ with the J and K sums replaced by integrals:

$$F_l(t)=\int_0^{\infty}dJ\int_{-J}^{J}dK\,2JP_{JK}(T)\sum_{J'K'}{}'\cos(E_{JK}-E_{J'K'})t\,\frac{(l-|K-K'|)!}{(l+|K-K'|)!}\left|P_l^{|K-K'|}(\cos\phi)\right|^2\begin{bmatrix} J & l & J' \\ K & K'-K & K'\end{bmatrix}^2\,, \tag{5}$$

where $$E_{JK}=(1/2I)J^2+(c/2I)K^2 \tag{6}$$

and $$c=(I-I_Z)/I_Z\,. \tag{7}$$

An expression for $F_l(t)$ can now be obtained from Eq. (5) when the limiting expressions of the Clebsch-Gordan coefficients for large J are substituted. In the case of $l=1$, the limiting expressions of various Clebsch-Gordan coefficients are[5]

$$\begin{bmatrix} J & 1 & J+1 \\ K & 0 & K\end{bmatrix}^2=\tfrac{1}{2}(1-x^2)\,,\qquad \begin{bmatrix} J & 1 & J \\ K & 0 & K\end{bmatrix}^2=x^2\,,\qquad \begin{bmatrix} J & 1 & J+1 \\ K & 1 & K+1\end{bmatrix}^2=\tfrac{1}{4}(1+x)^2\,,$$
$$\begin{bmatrix} J & 1 & J \\ K & 1 & K+1\end{bmatrix}^2=\tfrac{1}{2}(1-x^2)\,,\qquad \begin{bmatrix} J & 1 & J+1 \\ K & -1 & K-1\end{bmatrix}^2=\tfrac{1}{4}(1-x)^2\,, \tag{8}$$

where the variable $x=K/J$. Carrying out the J integration we find

$$F_1(t)=\cos^2\phi\,\tfrac{1}{2}(1+c)^{1/2}(Y_1+Y_2)+\sin^2\phi\,\tfrac{1}{4}(1+c)^{1/2}(Y_3+Y_4)\,, \tag{9}$$

where $$Y_1=-2/c\sqrt{1+c}+2/c\sqrt{c}\,\ln[\sqrt{(1+c)}+\sqrt{c}]\,,\qquad \text{if } c\geq 0$$
$$Y_1=-2/c\sqrt{1+c}+1/c\sqrt{-c}\,\sin^{-1}\{2[-c(1+c)]^{1/2}\}\,;\qquad \text{if } c\leq 0 \tag{10}$$

$$Y_2=\int_{-1}^{1}dx(1-x^2)\{[1+cx^2-\tau^2]/(1+cx^2)^{5/2}\}\exp[-\tau^2/2(1+cx^2)]\,, \tag{11}$$

$$Y_3=\int_{-1}^{1}dx(1-x^2)\{[1+cx^2-c^2x^2\tau]/(1+cx^2)^{5/2}\}\exp[-c^2x^2\tau^2/2(1+cx^2)]\,, \tag{12}$$

$$Y_4=\int_{-1}^{1}dx(1+x)^2\{[1+cx^2-(1+cx)^2\tau^2]/(1+cx^2)^{5/2}\}\exp[-(1+cx)^2\tau^2/2(1+cx^2)]\,, \tag{13}$$

with $\tau=(T/I)^{1/2}t$. This result was first obtained by St. Pierre and Steele using conditional distribution functions for orientations and angular momenta, and performing appropriate phase-space averages.[2] Equation (9) should be compared with the earlier expression[1]

$$F_1(t) = \cos^2\phi\, g(t) + \sin^2\phi\, \tfrac{1}{2}[1 + g(t)]\exp[(\tfrac{1}{2}c)(T/I)t^2] \;, \tag{14}$$

where $g(t)$ is the first-order correlation function for a linear molecule [Eq. (16)].

One can readily obtain corresponding expressions for linear and spherical rotors by taking appropriate limits. The linear rotor result is obtained by setting $I_z = 0$ and $\phi = 0$. In the limit $c \to \infty$, Eq. (9) reduces to

$$F_1(t) = \lim_{c \to \infty} \sum_{n=0}^{\infty} (-1)^n \left(\frac{\tau^2}{2}\right)^n (1+c)^{1/2} \int_{-1}^{1} dx (1-x^2) \left(\frac{1}{(1+cx^2)^{n+3/2}} - \frac{\tau^2}{(1+cx^2)^{n+5/2}}\right) . \tag{15}$$

The integral involved in the above equation is evaluated with the help of a recursion relation and, when the limit $c \to \infty$ is taken, we obtain

$$F_1(t) = M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\tau^2) e^{-\tau^2/2} \;, \tag{16}$$

where $M(a, b, x)$ is the Krummer's confluent hypergeometric function.[7] For spherical rotors, $c = 0$, and we obtain

$$F_1(t) = \tfrac{1}{3} + \tfrac{2}{3}(1 - \tau^2) e^{-\tau^2/2} \;. \tag{17}$$

Note that Eq. (14) is at best very restrictive since it does not reduce properly in the $c = 0$ limit. In Fig. 1, we show the behavior of $F_1(t)$ for symmetric, linear, and spherical rotors. The symmetric molecule result is appropriate to the case of ammonia.

Following the same procedure, we have derived $F_2(t)$ for a symmetric rotor. The result is

$$F_2(t) = [(3\cos^2\phi - 1)/2]^2 \, [\tfrac{1}{8}(1+c)^{1/2}] \, (Z_1 + Z_2 + Z_3) + \tfrac{3}{4}\cos^2\phi \sin^2\phi \, (1+c)^{1/2}(Z_4 + Z_5 + Z_6)$$
$$+ \tfrac{3}{64}\sin^4\phi \, (1+c)^{1/2} (Z_7 + Z_8 + Z_9) \;, \tag{18}$$

where

$$Z_1 = [(2c^2 + 21c + 27)/c^2(1+c)^{1/2}] - [(12c + 27)/c^2\sqrt{c}]\ln[(1+c)^{1/2} + \sqrt{c})] \,, \qquad \text{if } c \geq 0$$
$$Z_1 = [(2c^2 + 21c + 27)/c^2(1+c)^{1/2}] - [(12c + 27)/2c^2\sqrt{-c}]\sin^{-1}\{2[-c(1+c)]^{1/2}\} \,, \qquad \text{if } c \leq 0 \tag{19}$$

$$Z_2 = 12\int_{-1}^{1} dx\, x^2(1 - x^2)[(1 + cx^2 - \tau^2)/(1 + cx^2)^{5/2}]\exp[-\tau^2/2(1 + cx^2)] \;, \tag{20}$$

$$Z_3 = 3\int_{-1}^{1} dx (1 - x^2)^2[(1 + cx^2 - 4\tau^2)/(1 + cx^2)^{5/2}]\exp[-2\tau^2/(1 + cx^2)] \;, \tag{21}$$

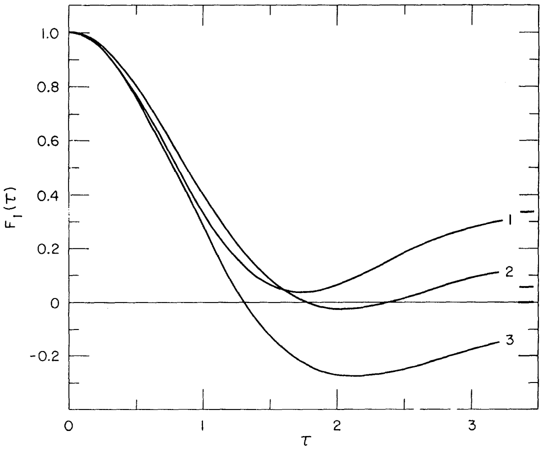

FIG. 1. Classical rotational correlation functions $F_1(\tau)$ for spherical (1), symmetric (2), and linear (3) molecules, where dimensionless time τ is $(T/I)^{1/2}t$. Curve 2 is for ammonia ($c = -0.365$, $\phi = 68°$). The asymptotic values of $F_1(\tau)$'s are shown by horizontal lines.

$$Z_4 = 3\int_{-1}^{1} dx\, x^2(1-x^2)[(1+cx^2-c^2x^2\tau^2)/(1+cx^2)^{5/2}]\exp[-c^2x^2\tau^2/2(1+cx^2)] \,, \tag{22}$$

$$Z_5 = \int_{-1}^{1} dx(1+x)^2(1-2x)^2\{[(1+cx^2)-(1+cx)^2\tau^2]/(1+cx^2)^{5/2}\}\exp[-(1+cx)^2\tau^2/2(1+cx^2)] \,, \tag{23}$$

$$Z_6 = \int_{-1}^{1} dx(1+x)^2(1-x^2)\{[(1+cx^2)-(2+cx)^2\tau^2]/(1+cx^2)^{5/2}\}\exp[-(2+cx)^2\tau^2/2(1+cx^2)] \,, \tag{24}$$

$$Z_7 = 3\int_{-1}^{1} dx(1-x^2)^2[(1+cx^2-4c^2x^2\tau^2)/(1+cx^2)^{5/2}]\exp[-2c^2x^2\tau^2/1+cx^2] \,, \tag{25}$$

$$Z_8 = 4\int_{-1}^{1} dx(1+x)^2(1-x^2)[(1+cx^2)-(1+2cx)^2\tau^2/(1+cx^2)^{5/2}]\exp[-(1+2cx)^2\tau^2/2(1+cx^2)] \,, \tag{26}$$

$$Z_9 = \int_{-1}^{1} dx(1+x)\{[1+cx^2-4(1+cx)^2\tau^2]/(1+cx^2)^{5/2}\}\exp[-2(1+cx)^2\tau^2/1+cx^2] \;. \tag{27}$$

This expression is also in agreement with the result given by St. Pierre and Steele.

The classical spectral density function $S_l(\omega)$ is defined as the Fourier transform of $F_l(t)$,

$$S_l(\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} F_l(t)\, e^{i\omega t}\, dt = \pi^{-1}\int_0^{\infty} F_l(t)\cos\omega t\, dt \,, \tag{28}$$

since $F_l(t)$ is an even function in t. We have obtained the following expression for $S_1(\omega)$ for a symmetric rotor:

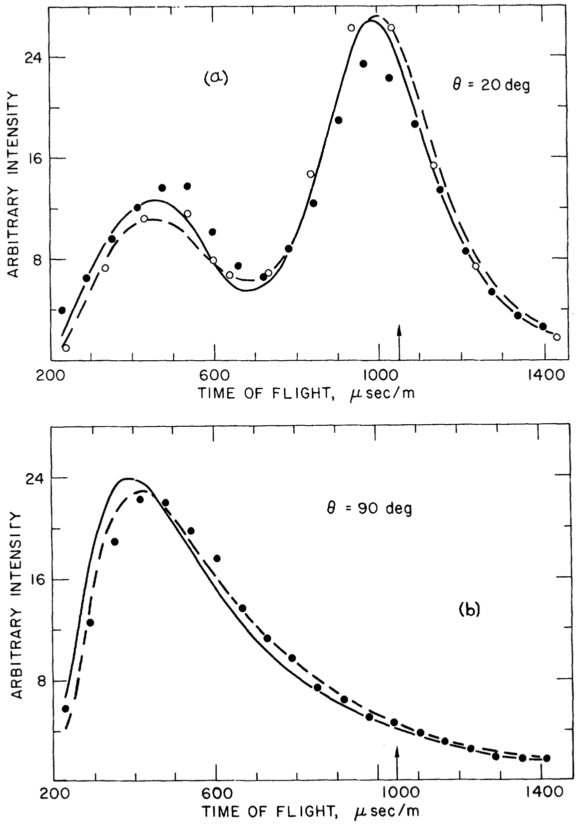

FIG. 2. Time-of-flight spectra of neutrons scattered by ammonia gas at $T = 295$ °K, experimental points (Ref. 9) (solid circles), theoretical spectra using Eqs. (9) and (14) (solid and dashed curves), and exact quantum-mechanical calculations (Ref. 10) (open circles). The arrow indicates the incident neutron energy of 4.87 MeV, and the spectra are all area normalized.

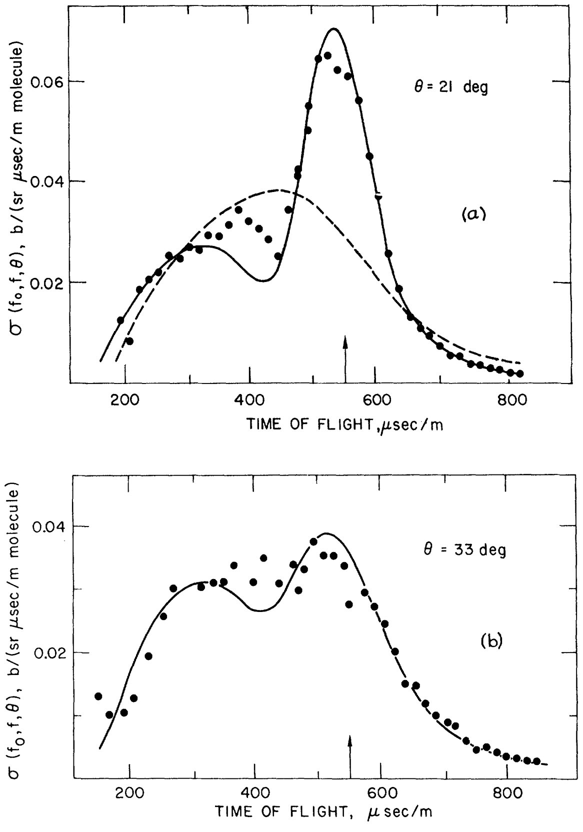

FIG. 3. Absolute time-of-flight cross section of water vapor at $T = 593$ °K for incident neutrons of 17.3 MeV, experimental points of W. Glaser, (Ref. 12) present calculations (solid curves), and results based on the Krieger-Nelkin model (Ref. 14) (dashed curve).

$$S_1(\omega)=\cos^2\phi\{Y_1\delta(\omega)+\tfrac{1}{2}(I/2\pi T)^{1/2}(1+c)^{1/2}\int_{-1}^{1}dx(1-x^2)\omega^{*2}\exp-(1+cx^2)(\tfrac{1}{2}\omega^{*2})\}$$
$$+\sin^2\phi\tfrac{1}{4}(I/2\pi T)^{1/2}(1+c)^{1/2}\{\int_{-1}^{1}dx[(1-x^2)/|cx|^3]\omega^{*2}\exp\{-\tfrac{1}{2}[(1+cx^2)/(cx)^2]\omega^{*2}\}$$
$$+\int_{-1}^{1}dx[(1+x)^2/(1+cx)^3]\omega^{*2}\exp(-\tfrac{1}{2}[(1+cx^2)/(cx)^2]\omega^{*2})\quad, \tag{29}$$

with $\omega^*=(I/T)^{1/2}\omega$. The higher-order spectral density functions can be obtained by substituting the corresponding expression for the rotational correlation function in Eq. (28). While the first- and second-order spectral density functions have been shown to be related to the appropriately normalized infrared and Raman band shapes,[8] the physical interpretation of the higher-order functions is not available.

We have applied Eq. (9) to the analysis of neutron-scattering measurements on gaseous ammonia and water vapor. The calculation is based on a Gaussian representation of χ_γ, and the procedure has been discussed in some detail in Ref. 1. In the case of NH_3, the time-of-flight distributions of neutrons scattered at 20° and 90° are shown in Fig. 2 along with the experimental points[9] and the earlier calculation [Eq. (14)]. In addition, exact quantum-mechanical results are available at 20°.[10] In the case of H_2O, the moments of inertia of the asymmetric molecule are $I_x=1.0243$, $I_y=1.9207$, and $I_z=2.9470\times10^{-40}$ g cm^2, and the H-O-H angle is 104° 27′.[11] Since rotational correlation functions for an asymmetric rotor have not yet been derived, we assume that H_2O can be treated as a symmetric molecule with moments of inertia $I'_x=I'_y=\frac{1}{2}(I_x+I_y)$, $I'_z=I_z$, and ϕ as half of the H-O-H angle. The comparison of absolute scattering intensities with experimental data[12] is shown in Fig. 3.[13] For the 21° scattering angle, we also include the spectrum computed using the Krieger-Nelkin model (effective mass 1.81).[14] The discrepancy in the vicinity of 400 μsec/m could possibly arise from experimental effects, such as multiple scattering or small amounts of moisture in the sample.

In summary, we note that the two methods of deriving classical rotational correlation functions, the use of quantum-mechanical results for the intermediate scattering function,[6] and the use of classical conditional distribution functions,[2] give identical results for freely rotating molecules. Model calculations which incorporate intermolecular torque effects are of interest, and for this purpose the approach of St. Pierre and Steele seems to be more appropriate.

ACKNOWLEDGMENT

We are grateful to W. Glaser for sending us his data on water vapor.

---

[*] Work performed under the auspices of the U.S. Atomic Energy Commission.

[†] Work supported by the National Science Foundation.

[1] A. K. Agrawal and S. Yip, Phys. Rev. 171, 263 (1968).

[2] A. G. St. Pierre and W. A. Steele, Phys. Rev. 184, 172 (1969).

[3] A. Rahman, J. Nucl. Energy 13, 128 (1961).

[4] In all subsequent equations, we use $\hbar=k_B=1$.

[5] M. E. Rose, Elementary Theory of Angular Momentum (John Wiley & Sons, Inc., New York, 1957).

[6] V. F. Sears, Can. J. Phys. 45, 237 (1967).

[7] Handbook of Mathematical Functions, edited by M. Abramowitz and I. A. Stegun (Dover Publications, Inc., New York, 1965).

[8] R. G. Gordon, J. Chem. Phys. 43, 1307 (1965).

[9] F. J. Webb, Proc. Phys. Soc. (London) 92, 912 (1967).

[10] G. Venkataraman, K. R. Rao, B. A. Dasannacharya, and P. K. Dayanidhi, Proc. Phys. Soc. (London) 89, 379 (1966).

[11] G. Herzberg, Molecular Spectra and Molecular Structure, Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., New York, 1950).

[12] W. Glaser (private communication).

[13] A. K. Agrawal, Trans. Am. Nucl. Soc. 12, 194 (1969).

[14] T. J. Kreiger and M. S. Nelkin, Phys. Rev. 106, 290 (1957).