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Magnetic Scattering of Slow Neutrons from O_2 Gas*

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A general expression is derived for magnetic scattering of slow neutrons from oxygen gas which takes account of molecular rotation. The scattering derived on the basis of Meckler's ground electronic wave function for O_2 is discussed. The validity of the static or semiclassical approximation is considered. Values are given for the total magnetic cross section in laboratory coordinates based on Meckler's wave function. The magnetic scattering does not appear to be sufficiently sensitive to changes in the wave function to distinguish in practice between different reasonable approximate wave functions.

I. INTRODUCTION

THE magnetic scattering of slow neutrons from paramagnetic O_2 has been considered as an experimental means of obtaining information about the (valence) electron distribution of the molecule.[1,2] Since the nuclear and magnetic scattering are independent, the experimental magnetic cross section may be obtained by subtracting the calculated nuclear cross section from the measured cross section. Halpern and Appleton have calculated the total nuclear cross section. In this paper a theoretical examination is made of the magnetic scattering, and the total magnetic cross section is calculated.

One might hope with either x-ray diffraction or neutron magnetic diffraction to obtain an electron distribution for the molecule from the Fourier transform of a scattering amplitude. The electron distribution measured is, of course, different for the two types of diffraction. In both cases one is immediately disappointed by the loss of information caused by molecular thermal rotational and translational motion. Neutrons of a monochromatic beam incident on a sample of gas see molecules with a variety of velocities, angular velocities, positions, and orientations (classically speaking). Assuming negligible correlation between molecules, the resultant scattering is given by averaging the cross section of one molecule with respect to these parameters. The situation is similar for an x-ray beam incident on the gas. An important distinction arises, however, from the difference in velocities of the incident particles. The speed of light is so great relative to molecular velocities and angular velocities, that a molecule appears to a photon to be stationary both in position and orientation as the photon passes by. Not so for a neutron of wavelength 1 angstrom whose speed is only 1.32×10^{-5} that of light. This added complication in the neutron case may be viewed as follows.

The ratio α of the time of transit of a neutron across a molecule to the period of molecular rotation gives a measure of how much the molecule rotates during the neutron's passage. By use of the equi-partition theorem for rotational motion, α is found to be about $\frac{1}{4}$ for O_2 gas at room temperature and incident neutrons of wavelength $\lambda=5$ A, a typical value in the range $(1\gtrsim\lambda\gtrsim20$ A) of experimental interest. This value of α indicates that the static (or semiclassical) approximation commonly used in x-ray scattering theory for treating the effects of molecular rotation may not be applicable to slow neutron scattering. The static approximation has been found satisfactory[3,4] under some circumstances for the nuclear scattering of slow neutrons from molecules. Here we are concerned with its validity for the magnetic scattering. The effect of translational motion of the molecules may be viewed in a similar way. The ratio of the root-mean-square molecular speed to the neutron speed gives a measure of the neutron-molecule relative velocities; for room temperature this ratio is $0.12\lambda(\mathrm{A})$. The translational motion of the molecules may thus also be expected to have an important bearing on the cross section.

The above qualitative discussion is from a classical viewpoint. Consider now the wave functions describing the molecule required for the quantum-mechanical treatment. We shall assume the molecule is in its ground electronic and vibrational levels. (For the gas at room temperature, the Boltzmann factor for the first excited vibrational level is 4×10^{-4}.) We neglect the zero-point vibration. The rotational levels are given by $1.44K(K+1)$ cm^{-1}, only odd-K levels being occupied because of the Bose statistics of the nuclei. The ρ-type tripling[5,6] of these levels arising from the spin-spin and spin-orbit terms in the Hamiltonian and the coupling of the spin with the rotational motion will be neglected. With this assumption the electronic and rotational motion become independent (except, of course, insofar as the electrons rotate with the molecule as a whole), and the electron spin of the molecule becomes free in orientation. Some of the above assumptions are considered again in Sec. IV. The molecular wave function may then be expressed

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[1] O. Halpern and G. L. Appleton, Phys. Rev. **90**, 869 (1953).

[2] H. Palevsky and R. M. Eisberg, Phys. Rev. **95**, 659 (1954).

[3] N. Z. Alcock and D. G. Hurst, Phys. Rev. **83**, 1100 (1951).

[4] J. A. Spiers, National Research Council (Canada) Report CRT-417 (April, 1949). (N.R.C. No. 1940) (unpublished).

[5] R. Schlapp, Phys. Rev. **51**, 342 (1937).

[6] J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

as a product of an electronic, a vibrational, and a rotational wave function, the first determined in the Born-Oppenheimer approximation for equilibrium internuclear distance $R=1.21$ A, the second represented by a δ function of the internuclear distance, and the third by normalized spherical harmonics with the internuclear orientation as argument. The electronic wave function is a ${}^3\Sigma_g{}^-$, and will be considered in more detail in Sec. III.

Based on wave functions of this type we derive in Sec. II a general expression for the Born approximation cross section of O_2 in center-of-mass coordinates for the magnetic scattering, and also the corresponding cross section formula in the static approximation. In Sec. III we derive from Meckler's ground level electronic wave function[7] for O_2 a simple expression for the spin density in terms of which the scattering is conveniently described. In Sec. IV use of the static approximation is justified for the magnetic scattering, and the insensitivity of the scattering to the form of the $2p\pi_\pm$ orbital of the wave function is discussed. The total magnetic cross section is evaluated in Sec. V.

II. MAGNETIC SCATTERING CROSS-SECTION FORMULAS

A parallel beam of unpolarized slow neutrons of definite wavelength is assumed to be incident on a sample of O_2 gas in thermal equilibrium. No correlation between the molecules being assumed, the cross section for the gas is the sum of the cross sections for the individual molecules. Double scattering is negligible. The cross section in center-of-mass coordinates for the magnetic scattering of an unpolarized neutron beam may be expressed in terms of the partial cross sections per initial state of the molecule,

$$\sigma_{ba}(\boldsymbol{\kappa})=(k'/k)d_a{}^{-1}\sum(\nu_b',\nu_a)(\mathbf{I}-\mathbf{ee}) \\ :(\nu_b'|\mathbf{P}|\nu_a)^*(\nu_b'|\mathbf{P}|\nu_a), \quad (1)$$

corresponding to incident neutrons of wave vector $\mathbf{k}$ scattered from a molecule initially in an energy level E_a. After scattering, the molecule is left with an energy E_b and the neutron with wave vector $\mathbf{k}'$, with k' determined by conservation of energy: $\hbar^2(k'^2-k^2)/2\mathfrak{m}=E_a-E_b$, where $\mathfrak{m}$ is the neutron-molecule reduced mass. The momentum transferred to the molecule is $\hbar(\mathbf{k}-\mathbf{k}')=\hbar\boldsymbol{\kappa}=\hbar\kappa\mathbf{e}$. The summation is over the degenerate states, denoted by ν_a and ν_b', of the energy levels E_a and E_b; d_a is the degeneracy of E_a. σ_{ba} is given in (1) in units of $[(\mathfrak{m}/m_p)(g_ne^2/2mc^2)]^2$; m_p is the proton mass, g_n the neutron g factor. $\mathbf{I}$ is the unit dyadic. The magnetic scattering operator $\mathbf{P}$ in (1) is the sum of a spin part $\mathbf{P}^{(S)}$ and an orbital part[8] $\mathbf{P}^{(L)}$:

$$\mathbf{P}^{(S)}(\boldsymbol{\kappa})=\sum_j\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_j)\mathbf{s}_j, \quad (2a)$$

$$\mathbf{P}^{(L)}(\boldsymbol{\kappa})=\sum_j\tfrac{1}{4}\{E(\boldsymbol{\kappa}\cdot\mathbf{r}_j)\mathbf{l}_j+\mathbf{l}_jE(\boldsymbol{\kappa}\cdot\mathbf{r}_j)\}, \quad (2b)$$

where

$$E(\boldsymbol{\kappa}\cdot\mathbf{r})=2\int_0^1\lambda\exp(i\lambda\boldsymbol{\kappa}\cdot\mathbf{r})d\lambda \\ \rightarrow 1 \quad\text{as}\quad \boldsymbol{\kappa}\rightarrow 0. \quad (3)$$

The position, spin, and orbital angular momentum operators of the jth electron are denoted by $\mathbf{r}_j$, $\mathbf{s}_j$, and $\mathbf{l}_j$. The cross section per initial state of a molecule with energy E_a is obtained by summing σ_{ba} over all levels E_b consistent with conservation of energy. This cross section is then averaged over all initial states weighted by the Boltzmann factor.

A typical molecular wave function, discussed in Sec. I, will be denoted by $Y_J{}^M(\mathbf{u})\psi_e{}^{M_S}(X_1',X_2',\cdots,X_{16}')$; the rotational wave function[9] $Y_J{}^M$ is a normalized spherical harmonic[10] referred to a frame of reference fixed in space; the unit vector $\mathbf{u}$ defines the orientation of the internuclear axis. $\psi_e{}^{M_S}$ is the ${}^3\Sigma_g{}^-$ ground electronic wave function with spin magnetic quantum number M_S; it is convenient to quantize the spin $\mathbf{S}$ with respect to the space reference frame; X_j' denotes the position and spin coordinates of the jth electron, the prime indicating that the space coordinates are referred to a reference frame fixed in the molecule. The degeneracy indices ν of (1) refer to M and M_S.

The components of the vectors in (2) are ordinarily defined with respect to the space frame. To evaluate the matrix elements of (1) it is convenient to express the $\mathbf{r}_j$ and $\mathbf{l}_j$ with respect to the molecular frame. Using the invariance of a scalar product under rotation of coordinate reference frame: $\boldsymbol{\kappa}\cdot\mathbf{r}=\boldsymbol{\kappa}'\cdot\mathbf{r}'$ and $\mathbf{e}\cdot\mathbf{P}^{(L)}=\mathbf{e}'\cdot\mathbf{P}^{(L)\prime}$ we may express the matrix element $(J'M'M_S'|\mathbf{P}^{(L)}(\boldsymbol{\kappa})|\times JMM_S)$ in terms of

$$\mathbf{f}^{(L)\prime}(\boldsymbol{\kappa}')=\delta(M_S',M_S)\int\psi_e{}^{M_S*}(X') \\ \times\sum_j\tfrac{1}{4}\{E(\boldsymbol{\kappa}'\cdot\mathbf{r}_j')\mathbf{l}_j'+\mathbf{l}_j'E(\boldsymbol{\kappa}'\cdot\mathbf{r}_j')\} \\ \times\psi_e{}^{M_S}(X')dX_e', \quad (4)$$

where the integral is over the electron coordinates and includes summation over spins; $\mathbf{f}^{(L)\prime}$ is independent of M_S. $\mathbf{f}^{(L)\prime}$ vanishes for a Σ state, and as a consequence the orbital interaction leads to no scattering. It is well known that the average orbital angular momentum vanishes for an orbitally nondegenerate level. The usual proof, based on time reversal symmetry, may be generalized to show that $\mathbf{f}^{(L)\prime}$ vanishes: denoting the Hermitian conjugate by †, we have

$$\mathbf{l}^\dagger=\mathbf{l}=-\mathbf{l}^*; \quad [\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})]^\dagger \\ =\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})=[\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})]^*,$$

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[7] A. Meckler, J. Chem. Phys. **21**, 1750 (1953).

[8] The convenient form of the orbital operator given here is due to G. T. Trammel, Phys. Rev. **92**, 1387 (1953).

[9] The total orbital angular momentum quantum number is commonly denoted by K. See, e.g., reference 6.

[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951).

and hence

$$\mathbf{P}^{(L)}(\boldsymbol{\kappa})^\dagger=\mathbf{P}^{(L)}(-\boldsymbol{\kappa})=-\mathbf{P}^{(L)}(\boldsymbol{\kappa})^*.$$

Upon dropping the primes for simplicity in (4), $\mathbf{f}^{(L)\prime}(\boldsymbol{\kappa}')$ becomes

$$\begin{aligned}\mathbf{f}^{(L)}(\boldsymbol{\kappa})&=\delta(M_S',M_S)\int\psi_e^*\mathbf{P}^{(L)}(\boldsymbol{\kappa})\psi_e dX_e\\&=-\delta(M_S',M_S)\int\psi_e\mathbf{P}^{(L)}(\boldsymbol{\kappa})\psi_e^* dX_e,\end{aligned}$$

and, since ψ_e can be chosen real, it follows that $\mathbf{f}^{(L)}$ vanishes.

The matrix elements of the spin scattering operator may be treated similarly in terms of the integral

$$\int\psi_e^{M_S'*}\textstyle\sum_j\exp(i\boldsymbol{\kappa}'\cdot\mathbf{r}_j')\mathbf{s}_j\psi_e^{M_S}dX_e'.$$

The operator $\mathbf{P}^{(S)}$ obeys vector type commutation relations[10] with respect to $\mathbf{S}=\sum_j\mathbf{s}_j$; i.e., $[P_x^{(S)},S_y]=i\hbar P_z$, etc. Consequently, the integral may be reduced to

$$(SM_S'|\mathbf{S}|SM_S)\left\{\int\psi_e^{S*}\textstyle\sum_j\exp(i\boldsymbol{\kappa}'\cdot\mathbf{r}_j')s_{jz}\psi_e^{S}dX_e'/S\right\}.$$

Equation (1) may now be simplified by introducing the latter and using the relation

$$\sum_{M_S',M_S}(\mathbf{I}-\mathbf{ee}):(M_S'|\mathbf{S}|M_S)^*(M_S'|\mathbf{S}|M_S)=\tfrac{2}{3}S(S+1)(2S+1).$$

Thus,

$$\begin{aligned}\sigma_{J'J}(\boldsymbol{\kappa})&=[(2S+1)(2J+1)]^{-1}(k'/k)\\&\quad\times\sum_{M',M,M_S',M_S}(\mathbf{I}-\mathbf{ee})\\&\quad:(J'M'M_S'|\mathbf{P}^{(S)}(\boldsymbol{\kappa})|JMM_S)^*\\&\quad\times(J'M'M_S'|\mathbf{P}^{(S)}(\boldsymbol{\kappa})|JMM_S)\\&=\tfrac{2}{3}S(S+1)(2J+1)^{-1}(k'/k)\\&\quad\times\sum_{M',M}|(J'M'|f(\boldsymbol{\kappa}')|JM)|^2,\end{aligned}\tag{5}$$

where

$$f(\boldsymbol{\kappa}')\equiv\int\psi_e^{S*}\textstyle\sum_j\exp(i\boldsymbol{\kappa}'\cdot\mathbf{r}_j')s_{jz}\psi_e^{S}dX_e'/S\tag{6a}$$

$$\rightarrow 1\quad\text{as}\quad\boldsymbol{\kappa}\rightarrow 0.$$

The integral of $\psi_e^{S*}\exp(i\boldsymbol{\kappa}'\cdot\mathbf{r}_j')s_{jz}\psi_e^S$ over all electron coordinates (including spin) except $\mathbf{r}_j'$ is independent of j, because of the antisymmetry of ψ_e in the electron coordinates. This allows $f(\boldsymbol{\kappa}')$ to be expressed as a Fourier transform,

$$f(\boldsymbol{\kappa}')=\int\exp(i\boldsymbol{\kappa}'\cdot\mathbf{r}')\rho(\mathbf{r}')d\tau',\tag{6b}$$

of a normalized spin density

$$\begin{aligned}\rho(\mathbf{r}')\equiv N\int&\psi_e^{S*}(X',X_2',X_3'\cdots,X_{16}')\\&\times s_z\psi_e^{S}(X',X_2',X_3'\cdots,X_{16}')d\sigma dX_2'\cdots,\ dX_{16}'/S,\end{aligned}\tag{7a}$$

$d\sigma$ denoting summation over spin; $\int\rho(\mathbf{r}')d\tau'=1$. The quantity ρ, and consequently f, has the symmetry of the molecule. In evaluating the matrix elements of (5) it is convenient to expand $f(\boldsymbol{\kappa}')$ in spherical harmonics:

$$f(\boldsymbol{\kappa}')=\sum_{l=0}^{\infty}(2l+1)i^lA_l(\kappa)P_l(\mathbf{e}'\cdot\mathbf{u}'),\tag{6c}$$

where $A_l(\kappa)$ is given by[11]

$$A_l(\kappa)\equiv\int P_l(\mathbf{e}'\cdot\mathbf{u}')f(\boldsymbol{\kappa}')d\mathbf{e}'/4\pi i^l\tag{8a}$$

$$=\int j_l(\kappa r')P_l(\mathbf{u}'\cdot\mathbf{r}'/r')\rho(\mathbf{r}')d\tau';\tag{8b}$$

or, if the spin density (7a) is expanded in spherical harmonics

$$\rho(\mathbf{r}')=\sum_{l=0}^{\infty}[(2l+1)/4\pi]\rho_l(r')P_l(\mathbf{u}'\cdot\mathbf{r}'/r'),\tag{7b}$$

by

$$A_l(\kappa)=\int_0^\infty j_l(\kappa r')\rho_l(r')r'^2dr'.\tag{8c}$$

Let $\mathcal{R}^{-1}$ denote a rotation which sends the space frame into the molecular frame. We choose the z axis of the molecular frame along $\mathbf{u}$ and the z axis of the space frame along $\mathbf{e}$; the coordinates of $\mathbf{e}$ and $\mathbf{u}'$ are then the same, namely (0,0,1) in Cartesian coordinates. Symbolically the coordinates of $\mathbf{u}$ may be described by $\mathbf{u}=\mathcal{R}^{-1}\mathbf{e}$ and the coordinates of $\boldsymbol{\kappa}'=\kappa\mathbf{e}'$ by $\mathbf{e}'=\mathcal{R}\mathbf{u}'$, or, since the coordinates of $\mathbf{e}$ and $\mathbf{u}'$ are identical, by $\mathbf{e}'=\mathcal{R}\mathbf{e}$. To facilitate the evaluation of the matrix elements

$$(J'M'|f(\boldsymbol{\kappa}')|JM)=\int Y_J^{M'*}(\mathcal{R}^{-1}\mathbf{e})f(\mathcal{R}\boldsymbol{\kappa})Y_J^M(\mathcal{R}^{-1}\mathbf{e})d\mathbf{u}\tag{9}$$

of (5), in which the integration is over all solid angle, it is desirable to have the same argument appearing in each factor of the integrand. The azimuthal direction of the x- (or y-) axis of the molecular frame may be chosen arbitrarily because of the cylindrical symmetry of the molecule. We make use of this freedom in defining $\mathcal{R}^{-1}$ as a rotation about an axis perpendicular to the plane of $\mathbf{e}$ and $\mathbf{u}$. Then, if θ, ϕ are the spherical coordinates of $\mathbf{u}=\mathcal{R}^{-1}\mathbf{e}$, θ, $\phi\pm\pi$ are the spherical coordinates of $\mathbf{e}'=\mathcal{R}\mathbf{e}$.

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[11] The P_l are Legendre polynomials; the j_l are spherical Bessel functions; $d\mathbf{e}'$ denotes the element of solid angle.

From the properties of the spherical harmonics it follows that

$$Y_J{}^M(\mathcal{R}^{-1}\mathbf{e})=Y_J{}^M(\theta,\phi)$$
$$=(-)^M Y_J{}^M(\theta,\,\phi\pm\pi)=(-)^M Y_J{}^M(\mathcal{R}\mathbf{e}),$$

so that the arguments in the factors of the integrand of (9) may be made the same. The cross section $\sigma_{J'J}$ will depend only on the magnitude of $\boldsymbol{\kappa}$. The average with respect to molecular orientations associated with $(J'M'|f|JM)$ is equivalent to an average over the orientations of $\boldsymbol{\kappa}$.

The summation in (5) may be carried out with the aid of the spherical harmonic addition theorem

$$\textstyle\sum_M Y_J{}^{M*}(\mathbf{u}_1)Y_J{}^M(\mathbf{u}_2)=(2J+1)P_J(\mathbf{u}_1\cdot\mathbf{u}_2)/4\pi \tag{10}$$

to yield

$$\sigma_{J'J}(\kappa)=\tfrac{2}{3}S(S+1)(2J'+1)(k'/k)$$
$$\times\int P_{J'}(\mathbf{u}_1\cdot\mathbf{u}_2)P_J(\mathbf{u}_1\cdot\mathbf{u}_2)f^*(\kappa\mathbf{u}_1)$$
$$\times f(\kappa\mathbf{u}_2)d\mathbf{u}_1d\mathbf{u}_2/(4\pi)^2. \tag{11}$$

Since $P_J(\mathbf{u}_1\cdot\mathbf{u}_2)$ is invariant under simultaneous rotation of $\mathbf{u}_1$ and $\mathbf{u}_2$, it follows from the orthogonality theorem for the irreducible representations of the rotation group that $\int P_{J'}(\mathbf{u}_1\cdot\mathbf{u}_2)P_J(\mathbf{u}_1\cdot\mathbf{u}_2)Y_{l'}{}^{m'*}(\mathbf{u}_1\cdot\mathbf{e})$ $Y_l{}^m(\mathbf{u}_2\cdot\mathbf{e})d\mathbf{u}_1d\mathbf{u}_2$ vanishes unless $l'=l$ and $m'=m$, and is independent of m for given l. This fact, together with the addition theorem (10), allows one to evaluate in terms of [12,13]

$$\int_{-1}^{1}P_{J'}(\mu)P_J(\mu)P_l(\mu)d\mu=[2/(2l+1)](J'J00|J'Jl0)^2$$

the type of integral obtained when (6c) is substituted into (11). The result is

$$\sigma_{J'J}(\kappa)=\tfrac{2}{3}S(S+1)(2J'+1)(k'/k)$$
$$\times\sum_{l=0}^{\infty}(J'J00|J'Jl0)^2A_l{}^2(\kappa). \tag{12}$$

Consider now two limiting cases for the cross section corresponding to large and small values of the ratio α (mentioned in Sec. I) of the transit time of the neutron to the period of molecular rotation. The case $\alpha\gg1$ is academic, but instructive: very cold neutrons are incident on a "gas" at very low temperature, and the molecules are supposed to have no translational motion. From a classical viewpoint a neutron sees many orientations of a molecule during transit.

$$f(\boldsymbol{\kappa}')=f(\mathcal{R}\boldsymbol{\kappa})=\int\exp(i\boldsymbol{\kappa}\cdot\mathcal{R}^{-1}\mathbf{r}')\rho(\mathbf{r}')d\tau'$$
$$=\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}')\rho(\mathcal{R}\mathbf{r}')d\tau'=\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})\rho(\mathcal{R}\mathbf{r})d\tau$$

may be regarded as a scattering amplitude for a stationary molecule, so that $|f(\boldsymbol{\kappa}')|^2$ gives the cross section (to within a constant factor). For $\alpha\gg1$, then, the amplitude should correspond to an f with the spin density ρ averaged uniformly over all orientations of the molecule, which is equivalent to averaging $f(\boldsymbol{\kappa})$ over all orientations of $\boldsymbol{\kappa}$; i.e., symbolically, the amplitude should be $\langle f(\boldsymbol{\kappa})\rangle$, and the cross section $|\langle f\rangle|^2$. The quantum analog has the molecule initially in its lowest rotational level, and an incident neutron has insufficient energy for inelastic scattering; i.e., $J'=J=0$. In agreement with the classical picture, we obtain

$$\sigma_{00}(\kappa)=\tfrac{2}{3}S(S+1)|\langle f\rangle|^2=\tfrac{2}{3}S(S+1)A_0{}^2(\kappa). \tag{13}$$

For $\alpha\ll1$, the *static* or *semiclassical* limiting case, each neutron sees an instantaneous picture of the molecule corresponding to a cross section $|f(\boldsymbol{\kappa}')|^2$, but the random orientations of the molecule require this to be averaged so that for the gas the cross section is $\langle|f|^2\rangle$. In the quantum analog one envisages such large values of k that k'/k may be replaced by unity in $\sigma_{J'J}$. Then, with the aid of the closure property for spherical

TABLE I. Determinants of the symmetry states. The normalized determinants $A,\cdots,\phi_f$ with $M_S=1$ are defined by the molecular orbitals on the principal diagonal; these consist of filled $1s\sigma$ and $2s\sigma$ orbitals accounting for eight of the sixteen electrons, the remaining orbitals being specified by the table, a + or − entry indicating that the space orbital is occupied by an electron with + or − spin. The space orbitals are labeled both in standard notation and in Meckler's notation. Meckler lists the nine ${}^3\Sigma_g{}^-$ symmetry states as eigenfunctions of S_z with eigenvalue $M_S=0$; these yield the ϕ_μ when operated on by $(S_x+iS_y)/\sqrt{2}$.

	$2p\sigma_g$ ϕ_0	$2p\pi_u{}^+$ ϕ_+	$2p\pi_u{}^-$ ϕ_-	$2p\pi_g{}^+$ χ_+	$2p\pi_g{}^-$ χ_-	$2p\sigma_u$ χ_0
A	+ −	+	+	+	−	+ −
B	+ −	+	−	+	+	+ −
C	+ −	+	+	−	+	+ −
D	+ −	−	+	+	+	+ −
E	+	+ −	−	+	+ −	+
F	+	+ −	+	−	+ −	+
G	+	+ −	+	+	+ −	−
H	−	+ −	+	+	+ −	+
I	+	+	+ −	+ −	−	+
J	+	−	+ −	+ −	+	+
K	+	+	+ −	+ −	+	−
L	−	+	+ −	+ −	+	+
ϕ_c	+ −	+ −	+ −	+	+	
ϕ_d	+ −	+	+	+ −	+ −	
ϕ_e		+ −	+ −	+	+	+ −
ϕ_f		+	+	+ −	+ −	+ −

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[12] See, e.g., Biedenharn, Blatt, and Rose, Revs. Modern Phys. **24**, 249 (1952) for a discussion of the vector addition coefficients $(j_1j_2m_1m_2|j_1j_2jm)$, and a convenient computational formula. Note that $P_{J'}P_J=\sum_{l=0}^{\infty}(J'J00|J'Jl0)^2P_l$.

[13] M. Hamermesh and J. Schwinger, Phys. Rev. **69**, 145 (1946) give an analogous derivation for the neutron-nuclear scattering from deuterium.

harmonics

$$\sum_J\sum_M Y_J^{M*}(\mathbf{u}_1)Y_J^M(\mathbf{u}_2)$$
$$=\sum_J(2J+1)P_J(\mathbf{u}_1\cdot\mathbf{u}_2)/4\pi=\delta(\mathbf{u}_1-\mathbf{u}_2),$$

the cross section per initial state for a molecule initially in level E_J becomes, from (5),

$$\sum_{J'}\sigma_{J'J}(\kappa)=\tfrac{2}{3}S(S+1)\langle|f(\boldsymbol{\kappa})|^2\rangle, \tag{14}$$

independent of J.

III. THE SPIN DENSITY

The spin density[14] $\rho(\mathbf{r})$ of Eqs. (7) contains all the information about the ground electronic wave function $\psi_e{}^S$ of the molecule relevant to the scattering problem. More generally, a spin density may be used to express in a convenient form matrix elements diagonal in S of any operator of the type[10] $\mathbf{F}=\sum_j h(\mathbf{r}_j)\mathbf{s}_j$: $(SM_S'|\mathbf{F}|SM_S)=(SM_S'|\mathbf{S}|SM_S)\int h(\mathbf{r})\rho(\mathbf{r})d\tau$. The spin scattering operator (2a) corresponds to choosing $h(\mathbf{r})=\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})$.

The normal O_2 electronic level is a ${}^3\Sigma_g{}^-$. Meckler[7] approximates $\psi_e{}^S$ for this level by a linear combination of nine symmetry states of ${}^3\Sigma_g{}^-$ symmetry, each a linear combination of Slater determinants of (orthonormal) molecular orbitals, the orbitals being approximated by linear combinations of atomic orbitals. The molecular space orbitals for each determinant are chosen from the set

$$1s\sigma_g,\ 1s\sigma_u,\ 2s\sigma_g,\ 2s\sigma_u,\ 2p\sigma_g,\ 2p\pi_u{}^\pm,\ 2p\pi_g{}^\pm,\ 2p\sigma_u.$$

At normal internuclear distance the one-electron energies of the orbitals increase from left to right in the list. We write Meckler's $\psi_e{}^S$ as

$$\psi=\sum_{\mu=a}^{i} c_\mu\phi_\mu \quad \Big(\sum_{\mu=a}^{i} c_\mu{}^2=1\Big), \tag{15}$$

where, in terms of the determinants specified in Table I, the symmetry states ϕ_μ are given by

$$\begin{aligned}\phi_a&=\tfrac{1}{2}(A+B-C-D),\\ \phi_b&=\tfrac{1}{2}(B+C-A-D),\\ \phi_g&=2^{-\frac{3}{2}}(E+G-F-H+J+K-I-L),\\ \phi_h&=2^{-\frac{3}{2}}(F+G-E-H+I+K-J-L),\\ \phi_i&=2^{-\frac{3}{2}}(E+F-G-H+I+J-K-L),\end{aligned} \tag{16}$$

and the one-determinant symmetry states ϕ_c, ϕ_d, ϕ_e, and ϕ_f. The symmetry state ϕ_c, which corresponds to the molecular orbital solution, predominates at normal internuclear distance $(1-|c_c|^2=0.05)$. The set of orbitals for ϕ_c gives the lowest value for the sum of one-electron energies.

TABLE II. Values of the C's of Eqs. (17) as a function of internuclear distance for Meckler's O_2 normal ${}^3\Sigma_g{}^-$ electronic wave function. The importance of the one-determinant molecular orbital solution ϕ_c in Meckler's wave function is indicated in the last row. Note that $\Sigma_i C_i=1$.

R(a.u.)	2.0	2.5	4.0	∞
C_1	−0.0009	−0.0018	0.2212	1/4
C_2	0.0180	0.0394	0.2590	1/4
C_3	0.9816	0.9591	0.2980	1/4
C_4	0.0013	0.0033	0.2213	1/4
$c_c{}^2$	0.9700	0.9347	0.1902	1/8

In case, as here, $\psi_e{}^S$ is expressed as a linear combination of determinants of orthonormal orbitals, $\rho(\mathbf{r})$ is a quadratic form in the orbitals, the cross terms (overlap terms) arising from products of determinants differing by one orbital. No overlap terms appear in ρ for Meckler's $\psi_e{}^S$, since all determinants involved differ by at least two orbitals. This follows from the fact that the $1s\sigma$ and $2s\sigma$ orbitals are always filled and no two space orbitals outside the $1s\sigma$ and $2s\sigma$ are of the same symmetry; changing the symmetry of only one space orbital would change the symmetry of $\psi_e{}^S$.

The result of inserting (15) into (7a) is, in terms of the molecular space orbitals φ,

$$\rho(\mathbf{r})=C_1|\varphi(2p\sigma_g)|^2+C_2|\varphi(2p\pi_u{}^\pm)|^2$$
$$+C_3|\varphi(2p\pi_g{}^\pm)|^2+C_4|\varphi(2p\sigma_u)|^2, \tag{17a}$$

where

$$\begin{aligned}\mathrm{C}_1&=\alpha+\beta+\gamma-\delta,\\ C_2&=\tfrac{1}{2}|c_a-c_b|^2+c_d{}^2+c_f{}^2-\alpha+\beta+\gamma+\delta,\\ C_3&=\tfrac{1}{2}|c_a+c_b|^2+c_c{}^2+c_e{}^2+\alpha-\beta+\gamma+\delta,\\ C_4&=\alpha+\beta-\gamma+\delta,\\ \alpha&=\tfrac{1}{8}(c_g-c_h+c_i)^2,\quad \beta=\tfrac{1}{8}(-c_g+c_h+c_i)^2,\\ \gamma&=\tfrac{1}{8}(c_g+c_h-c_i)^2,\quad \delta=\tfrac{1}{8}(c_g+c_h+c_i)^2.\end{aligned} \tag{17b}$$

Note that $\sum_i C_i=1$. The coefficients c_μ are given by Meckler as a function of internuclear distance; corresponding values of the coefficients C_i are given in Table II. At equilibrium distance the contribution of the $2p\sigma$ orbitals may be neglected, and we may write $C_2+C_3=1$. With the $2p_\pm$ atomic orbitals at $-\mathbf{R}/2$ and $\mathbf{R}/2$ denoted by ϕ and ϕ', and the overlap integral $\int\phi^*\phi'd\tau$ by Δ, the spin density (17a, b) reduces to

$$\rho(\mathbf{r})=a(|\phi|^2+|\phi'|^2)+b2\phi^*\phi', \tag{18}$$

with

$$a=\frac{1+(2C_3-1)\Delta}{2(1-\Delta^2)},\quad b=-\frac{(2C_3-1)+\Delta}{2(1-\Delta^2)}. \tag{18'}$$

These reduce to $a=-b=\tfrac{1}{2}$ for the molecular orbital solution together with $\Delta=0$. For $C_3=0.97$ (interpolation for $R=2.28$ from Table II) and reasonable values of Δ, a and $-b$ may be larger by as much as about 30 percent. (For Meckler's Gaussian, Duncanson-Coulson's hydro-

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[14] Henceforth we drop the primes and refer all coordinates to the molecular frame.

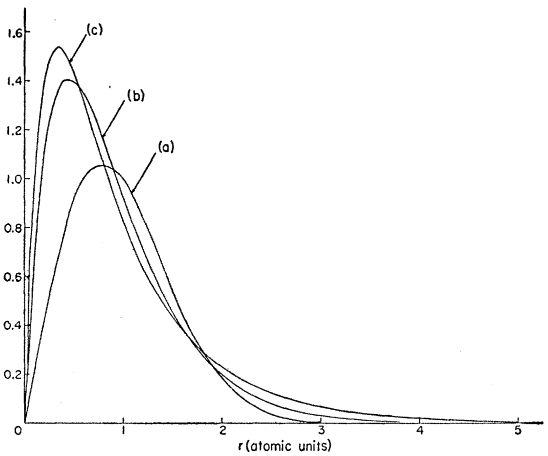

FIG. 1. $R(r)$ for normalized atomic $2p_{\pm}$ orbitals $R(r)Y_1^{\pm1}(\theta,\phi)$ of the (a) Meckler-Gaussian (see reference 7), (b) hydrogenic (see reference 15) ($Z=4.44$), and (c) Hartree-Fock (see reference 16) types.

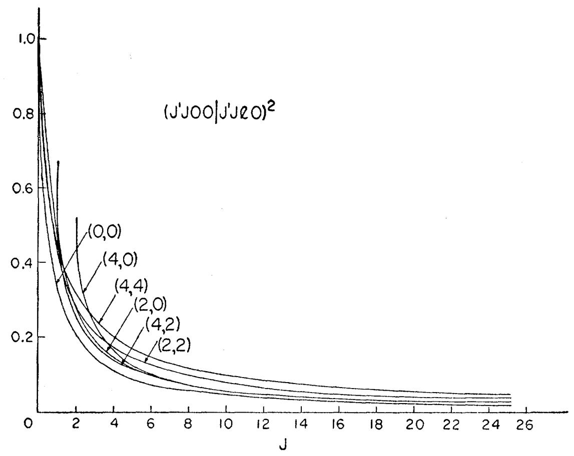

FIG. 2. A plot of $(J'J00|J'Jl0)^2$ vs J. These functions are here defined only for integral values J and J'. The smooth curves are drawn for clarity. The curves are labeled by $(l,\Delta J)$ where $\Delta J = J'-J$.

genic,[15] and Hartree-Fock[16] orbitals, Δ is 0.125, 0.158, and 0.244, respectively, at $R=2.28$ a.u.) The radial wave functions for these orbitals are plotted in Fig. 1 for comparison. If Hartree-Fock or other reasonable types of atomic orbitals were used in Meckler's calculation in place of his Gaussian-type orbital, the c_μ might differ somewhat, but it seems unlikely that the C's of (17) would change significantly.

IV. MAGNETIC CROSS SECTION IN CENTER-OF-MASS COORDINATES

From a study of computed curves of the $A_l(\kappa)$, which depend on the spin density through $f(\mathbf{\kappa})$, two main conclusions may be drawn. First, the error in the cross section associated with the static approximation may generally be neglected. This is fortunate, since use of the static approximation allows very great reduction in the amount of computing required to obtain the cross section. Second, the cross section is rather insensitive to the form of the radial part of the oxygen $2p$ atomic orbital. This is unfortunate in that it means the scattering does not provide a sensitive probe for the electron distribution of the molecule.

The validity of the static approximation (14) is based on the smallness of the inelastic scattering relative to the elastic scattering. $(J'J00|J'Jl0)$ vanishes for $J'+J+l$ odd and for $|J'-J|>l$. From the inversion symmetry of the molecule it follows that A_l vanishes for l odd, and hence only J' and J for even $|J'-J|$ are involved. (This is independently a consequence of the symmetry of the wave function under exchange of nuclei if the molecule contains only one isotope.) Some values of $(J'J00|J'Jl0)^2$ are plotted in Fig. 2. It follows that if $A_l=0$ for $l\neq 0$, i.e., if the spin density is spherically symmetrical, the scattering is purely elastic. In this case the static approximation is justified, since $\sigma_{J'J}=\delta_{J'J}\sigma_{JJ}$, so that replacing k'/k by unity, as required in the static approximation, has rigorously no effect on $\sigma_{J'J}$, and including contributions $\sigma_{J'J}$ to the scattering from transitions for which energy cannot be conserved, also required by the static approximation, also has no effect. The actual scattering approaches this ideal case. The $A_l(\kappa)$ derived from Meckler's ground electronic wave function (15) are plotted in Fig. 3. Denoting the maximum value of $|A_l(\kappa)|$ for given l by $|A_l|_m$, we may use the smallness of $(|A_l|_m/|A_0|_m)^2=|A_l|_m^2$ as a criterion for the validity of the static approximation; if this ratio vanishes for all $l>0$, we have the ideal case discussed above. It may be seen from Table III that this criterion is quite well satisfied. It is true that this criterion is no longer satisfactory if values of κ for which $|A_0(\kappa)|\approx|A_2|_m$ are of particular interest, e.g., in differential cross section measurements for sufficiently large scattering angles and/or small incident wave lengths; such cases, which involve smaller scattered intensities (especially relative to the nuclear scattering), are likely to be of less experimental interest in the near future.

Another indication that use of the static approximation will lead to satisfactory results comes from a comparison of $\langle|f|^2\rangle$ and $|\langle f\rangle|^2$ discussed in Sec. II. These differ appreciably only as κ approaches the tail region (see Fig. 4), and since they represent two limiting cases for the ratio α, one might expect intermediate cases not to differ significantly. We may also interpret $|\langle f\rangle|^2$ as the rigorous scattering if $A_l=0$ for $l\neq 0$, and the difference between $\langle|f|^2\rangle$ and $|\langle f\rangle|^2$ as taking approximate account of the nonvanishing of

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[15] W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. Edinburgh **A62**, 37 (1944).

[16] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1939). To calculate Δ we used the analytic fit of the radial function for the oxygen ^1S given by P. O. Löwdin, Phys. Rev. **90**, 120 (1953), together with formulas from C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

these A_l for $l \neq 0$, i.e., the nonsphericity of the spin density.

For the nuclear scattering one finds a partial cross section[13,3] “$\sigma_{J'J}$” similar to (12). The κ dependence of the nuclear partial cross section is obtained by replacing the electron spin density by the density of nuclear matter, i.e., δ functions at the equilibrium nuclear positions (if vibration is ignored): $f(\boldsymbol{\kappa})$ and $A_l(\kappa)$ reduce simply to $\cos(\boldsymbol{\kappa}\cdot\mathbf{R}/2)$ and $\frac{1}{2}[1+(-)^l]j_l(\kappa R/2)$. From a comparison of the A_l for the magnetic and nuclear scattering plotted in Fig. 3, it is apparent that the static approximation has greater validity in the magnetic case. There are two reasons for this. First, the spin density is widely distributed radially so that its Fourier transform falls off more rapidly with κ than in the nuclear case where the density is finite only on one spherical shell. Second, the spin density is more spherically distributed than the nuclear density, as indicated by (7b) and (8c).

The A_l were computed with a hydrogenic $2p_\pm$ atomic orbital with effective nuclear charge[15] $Z=4.44$ in (18) replacing Meckler's Gaussian orbital (but maintaining $C_3=0.97$). The A_l are very similar in form for the two types of orbitals, both behaving roughly like damped spherical Bessel functions (see Fig. 3), the damping being in agreement with the extensive radial distribution of the spin density. Table III indicates the relative positions of the main peaks for each l. The A_0's differ by at most 0.03 for the two orbitals (see Fig. 3). It appears unlikely that the cross sections determined from these two orbitals could be experimentally distinguished at present. It may be of interest that the contribution to A_0 from the b or overlap part of (18) is relatively small; it has the general shape of A_0 itself, but falls off from about -0.15 at $\kappa=0$ crossing the axis at about $\kappa R/2=3.5$ and 7.

As an experimental means of distinguishing between various reasonable types of molecular wave functions of O_2, the scattering of neutrons proves to be of little use. We see that even before the blurring effect of the translational motion of the molecules is taken into account, the magnetic scattering differs very little for the two types of $2p_\pm$ orbitals assumed. Our original assumptions for the molecular wave function disregarded the zero-point vibration (for which the rms fractional

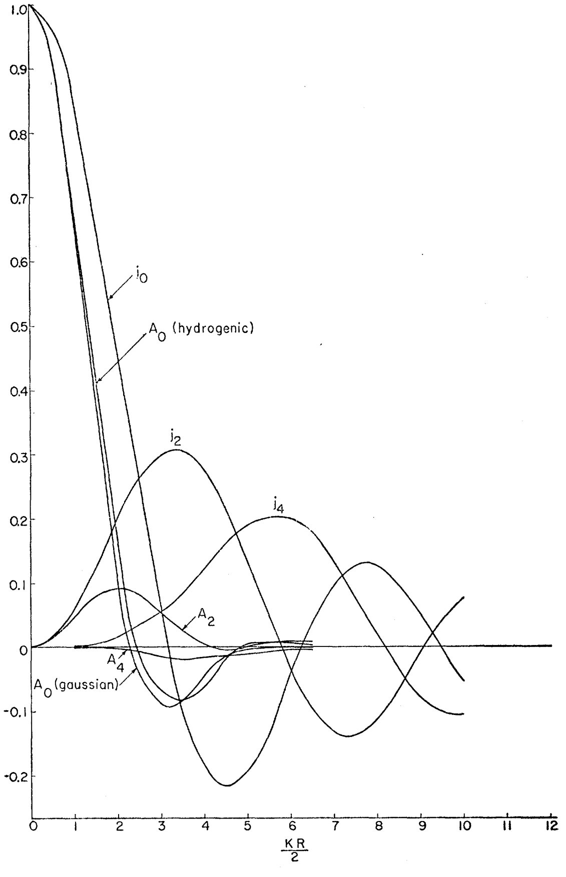

FIG. 3. The coefficients A_l, $l=0$, 2, 4, of Eqs. (8) for Meckler's ground electronic wave function vs $\kappa R/2$ are plotted together with j_l, $l=0$, 2, 4, the corresponding coefficients for the nuclear scattering. The small effect on the magnetic scattering of replacing the Gaussian $2p$ atomic orbital of Meckler's wave function by a hydrogenic orbital ($Z=4.44$) may be seen by comparing the A_0's plotted for the two orbitals.

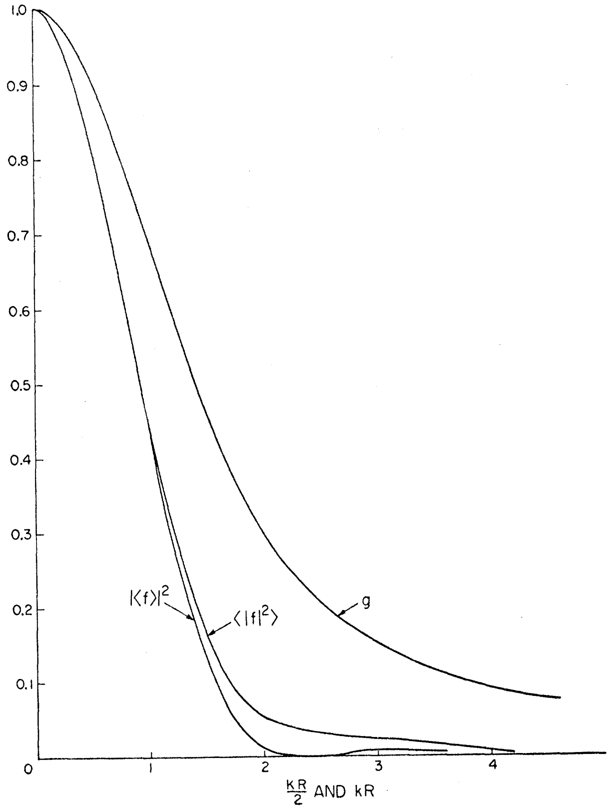

FIG. 4. The spherical averages $\langle|f|^2\rangle$ and $|\langle f\rangle|^2$ of f vs $\kappa R/2$ for Meckler's ground electronic wave function. Also plotted is the form g of the total magnetic cross section in center-of-mass coordinates vs kR.

TABLE III. The extreme values of A_l and the corresponding arguments for $l=0, 2, 4, 6, 8$ derived (a) from Meckler's Gaussian, and (b) from hydrogenic (see reference 15) $(Z=4.44)2p_{\pm}$ atomic orbitals.

	l	0	2	4	6	8
(a)	$(A_l)_{\text{ext}}$	1.00	0.09	−0.017	−0.009	−0.002
	$(\kappa R/2)_{\text{ext}}$	0.0	2	3.8	4.4	5
(b)	$(A_l)_{\text{ext}}$	1.00	0.11	−0.005	−0.0072	−0.003
	$(\kappa R/2)_{\text{ext}}$	0.0	2.2	3.2	4.8	6.5

change of internuclear distance is only 0.03), and also the couplings of the electronic spin leading to fine structure[17] in the rotational levels. One would hardly expect that if these were taken into account the change in scattering, even in center-of-mass coordinates, would be greater than that obtained if reasonable changes are made in the $2p_{\pm}$ orbitals.

V. TOTAL MAGNETIC CROSS SECTION

From the partial cross sections $\sigma_{J'J}(\kappa)$ of (12) one could in principle compute the distribution in angle and energy of the scattered neutrons in the laboratory frame of reference.[18] Here we shall be concerned with the total cross section in the laboratory frame derived from the static approximation expression (14) together with Meckler's wave function (15). In accordance with the assumption of nearly elastic scattering involved in the static approximation, we set $\kappa=2k\sin(\theta/2)$, where θ is the scattering angle. By integrating (14) over all solid angle, we obtain for the total cross section in center-of-mass coordinates, in units of $\frac{2}{3}S(S+1)\times[(\mathfrak{m}/m_p)(g_ne^2/2mc^2)]^2=0.3650\times10^{-24}$ cm², the expression

$$\sigma(k)=\int\langle|f(\boldsymbol{\kappa})|^2\rangle\sin\theta d\theta d\phi=(2\pi/k^2)\int_0^{2k}\langle|f|^2\rangle\kappa d\kappa \tag{19}$$

$$\rightarrow 4\pi \quad \text{as} \quad k\rightarrow 0.$$

TABLE IV. Total magnetic cross section σ per molecule of oxygen gas for neutrons of incident wavelength λ. In the limit of infinite wavelength the relative motion of the neutrons and molecules depends only on the molecular motion, and σ/λ approaches a limit independent of λ, which for $T=20$°C is 0.361 barn/angstrom.

λ (angstroms)	1	2	3	4	5	7.5	10	15	20	30
σ (barns)	0.130	0.490	0.981	1.516	2.015	3.054	3.96	5.76	7.52	11.09

The required integration was carried out numerically in terms of the more convenient integration variable $\kappa R/2$. The resulting function is plotted in Fig. 4. The transformation of the cross section in center-of-mass coordinates to laboratory coordinates is based on the principle that the number of neutrons scattered per unit time is independent of the Newtonian reference frame. Averaging[19] over a distribution of molecular velocities appropriate to a gas temperature of 20°C led to values of the total cross section given in Table IV. The agreement with experiment[20] is to within the experimental error.

The author is indebted to Dr. H. Palevsky and Dr. L. van Hove for several interesting discussions concerning this work. A large part of the computation was done by Miss Edith Moss. I am pleased to express my appreciation to others of the Solid-State and Molecular Theory Group at M. I. T. and especially to Professor J. C. Slater for the stimulating atmosphere I have enjoyed during the course of this work.

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[17] The over-all fine structure splitting for each rotational level of interest is about 2 cm^{-1} corresponding to a neutron wavelength of 15A. These splittings will not affect the scattering, at least to the extent that the split levels are equally populated, and that scattering corresponding to transitions among them may be regarded as elastic.

[18] For a detailed discussion of the required transformations see reference 4.

[19] The same procedure is used in references 12 and 1. In the present case the integrals were carried out numerically.

[20] H. Palevsky and R. M. Eisberg (to be published).