

is always a possibility of the lattice restriction of the Compton process due to the total Bragg reflection condition of the recoil electrons according to formula (4). Considering the above facts, it is reasonable to argue that the characteristic modified lines would be best expected at small angles of scattering because the other normal channels of Compton interaction with both free and bound electrons are highly restricted at small angles of scattering.

#### ACKNOWLEDGMENTS

The author is grateful to Professor Pol Duwez for providing him with the research facilities in his laboratory and for his great interest in the particular problem and his helpfulness. Thanks are due to Dr. F. S. Buffington for going through the manuscript. The author is grateful to Professor J. W. M. DuMond for his encouragement and to Professor R. P. Feynman for valuable discussions.

## Multiple Scattering of Neutrons in the Static Approximation

J. H. FERZIGER AND A. LEONARD\*

*Nuclear Engineering Laboratory, Stanford University, Stanford, California*

(Received June 20, 1962; revised manuscript received August 27, 1962)

It is shown that, within the static approximation, the neutron diffraction pattern from a sample can be interpreted in terms of multiple particle correlation functions. In particular, the relation between double scattering and the three-particle correlation function is derived. Although the formula given cannot be formally inverted to give the three-particle correlation function, it may be useful for making corrections for multiple scattering in experiments.

#### INTRODUCTION

MUCH work has been done in the areas of elastic scattering of neutrons and x-ray diffraction from both solids and liquids, dating to the early work of Zernike and Prins.<sup>1</sup> It is readily demonstrated by means of the first Born approximation that the diffraction pattern can be interpreted in terms of the two-particle time-independent correlation function. More recently, Van Hove<sup>2</sup> and others have shown how inelastic neutron scattering may be described in terms of a time-dependent two-particle correlation function.

It is well known that this relation between the two-particle correlation function and the single-scattering diffraction pattern arises from the interference of the waves scattered from different nuclei. If, however, a neutron makes more than one collision in a sample, the diffraction pattern should be sensitive to the positions of more than two nuclei. For example, the pattern arising from the interference between singly scattered neutrons and twice scattered neutrons can be expected to be related to the three- and four-particle distribution functions.

In this paper the above statement is proven and it is shown how higher order correlation functions are related to higher order multiple scattering. Unfortunately, the results derived do not enable one to calculate the three-particle correlation function from the results of a diffraction experiment. The converse, however, is

true and the results may be useful for estimating the contribution of multiple scattering to the observed diffraction patterns. Thus, a simple correction for multiple scattering effects can be made.

#### THE SECOND BORN APPROXIMATION

Using a semiclassical approach and assuming that the nuclei of the scatterer are alike and stationary, the second Born (double scattering) approximation to the scattering cross section can be written

$$\sigma(\theta) = \left| \sum_n a_n e^{i\mathbf{K} \cdot \mathbf{r}_n} + \sum'_{n,m} a_n a_m e^{i\mathbf{k} \cdot \mathbf{r}_m} e^{-i\mathbf{k}' \cdot \mathbf{r}_n} \frac{e^{i\mathbf{k}|\mathbf{r}_n - \mathbf{r}_m|}}{|\mathbf{r}_n - \mathbf{r}_m|} \right|^2, \quad (1)$$

where  $\mathbf{k}$ =incoming wave vector,  $\mathbf{k}'$ =outgoing wave vector,  $\mathbf{K}=\mathbf{k}-\mathbf{k}'$ =scattered wave vector (momentum transfer vector),  $\mathbf{r}_n$ =position vector of the  $n^{\text{th}}$  nucleus, and the prime on the summation means that the  $m=n$  terms are to be omitted from the sum. The square of the first term in the brackets in Eq. (1) is known to be related to the two-particle correlation function.

Restricting our attention now to the cross-product term, we have

$$\sum_l a_l e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_l} \sum'_{m,n} a_m a_n e^{i\mathbf{k} \cdot \mathbf{r}_m} e^{-i\mathbf{k}' \cdot \mathbf{r}_n} \frac{e^{i\mathbf{k}|\mathbf{r}_n - \mathbf{r}_m|}}{|\mathbf{r}_n - \mathbf{r}_m|} + \text{c.c.} \quad (2)$$

Assuming the scattering lengths to be uncorrelated (i.e., random spin and isotope disorder) the first term of

\* Atomic Energy Commission Fellow.

<sup>1</sup> F. Zernike and J. Prins, *Z. Physik* **41**, 184 (1927).

<sup>2</sup> L. Van Hove, *Phys. Rev.* **95**, 249 (1954).

expression (2) can be broken into a sum with  $l \neq m \neq n$  and a sum with  $l = m$  or  $n$ :

$$\begin{aligned} \langle a \rangle^3 \sum'_{l,m,n} \int \int \int d^3r d^3r' d^3r'' & e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}'} e^{-i\mathbf{k}' \cdot \mathbf{r}''} \\ & \times \frac{e^{i\mathbf{k}|\mathbf{r}'-\mathbf{r}''|}}{|\mathbf{r}'-\mathbf{r}''|} \delta(\mathbf{r}-\mathbf{r}_l) \delta(\mathbf{r}'-\mathbf{r}_m) \delta(\mathbf{r}''-\mathbf{r}_n) \\ & + \langle a^2 \rangle \langle a \rangle \sum'_{m,n,o} \int \int d^3r d^3r' (e^{i\mathbf{k} \cdot (\mathbf{r}'-\mathbf{r})} + e^{i\mathbf{k}' \cdot (\mathbf{r}'-\mathbf{r})}) \\ & \times \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \delta(\mathbf{r}-\mathbf{r}_m) \delta(\mathbf{r}'-\mathbf{r}_n), \end{aligned} \quad (3)$$

but, by definition,<sup>3</sup>

$$\begin{aligned} \sum'_{l,m,n} \delta(\mathbf{r}-\mathbf{r}_l) \delta(\mathbf{r}'-\mathbf{r}_m) \delta(\mathbf{r}''-\mathbf{r}_n) &= \rho g^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''), \\ \sum'_{m,n} \delta(\mathbf{r}-\mathbf{r}_m) \delta(\mathbf{r}'-\mathbf{r}_n) &= \rho g^{(2)}(\mathbf{r}, \mathbf{r}'), \end{aligned} \quad (4)$$

where  $g^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$  is the three-particle correlation function, i.e., the probability (per unit volume at  $\mathbf{r}'$  and  $\mathbf{r}''$ ) that, given a particle at  $\mathbf{r}$ , there be particles at  $\mathbf{r}'$  and  $\mathbf{r}''$ ; and  $g^{(2)}(\mathbf{r}, \mathbf{r}')$  is the more familiar two-particle correlation function.<sup>3</sup>

Clearly, in a fluid, the particle correlation functions are dependent only on the interparticle distances or  $|\mathbf{r}-\mathbf{r}'|$ ,  $|\mathbf{r}'-\mathbf{r}''|$ , and  $|\mathbf{r}-\mathbf{r}''|$  for  $g^{(3)}$  and  $|\mathbf{r}-\mathbf{r}'|$  for  $g^{(2)}$ .

If we let

$$\begin{aligned} \mathbf{x} &= \mathbf{r}' - \mathbf{r}'', \\ \mathbf{y} &= \mathbf{r} - \mathbf{r}'', \\ \mathbf{z} &= \mathbf{y} - \mathbf{x} = \mathbf{r}' - \mathbf{r}, \end{aligned}$$

expression (3) becomes

$$\begin{aligned} \rho \langle a \rangle^3 \int \int \int d^3x d^3y d^3z & e^{i\mathbf{k} \cdot \mathbf{x}} e^{i\mathbf{K} \cdot \mathbf{y}} \frac{e^{i\mathbf{k} \cdot \mathbf{z}}}{x} g^{(3)}(x, y, |\mathbf{x}-\mathbf{y}|) \\ & + \rho \langle a^2 \rangle \langle a \rangle \int \int d^3r d^3z (e^{i\mathbf{k} \cdot \mathbf{z}} + e^{i\mathbf{k}' \cdot \mathbf{z}}) \frac{e^{i\mathbf{k} \cdot \mathbf{z}}}{z} g^{(2)}(z), \end{aligned} \quad (5)$$

where

$$g^{(3)}(x, y, |\mathbf{x}-\mathbf{y}|) = g^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''), \quad g^{(2)}(z) = g^{(2)}(\mathbf{r}, \mathbf{r}').$$

Six of the nine integrations indicated in the first term above and five of six integrations in the second term may be carried out without a knowledge of the correlation functions involved. In the first term these integrations are over the coordinates of three particles constrained to a triangle of sides  $x$ ,  $y$ , and  $|\mathbf{x}-\mathbf{y}|$ . In the second term, the integrations are over the coordinates of two particles with the constraint that they be a fixed distance apart.

Finally, a spherical harmonics expansion of the first two exponentials in the integrand of the first term of expression (5) and subsequent integration gives for expression (2) [(5) plus c.c.],

$$\begin{aligned} 32\pi^2 \rho V \langle a \rangle^3 \int_0^\infty \int_0^\infty \int_0^\pi x^2 dx y^2 dy \sin \theta d\theta \sum_{l=0}^\infty (-1)^l P_l(\cos \theta) \\ P_l(\cos \gamma) j_l(Ky) j_l(kx) \frac{\cos kx}{x} g^{(3)}(x, y, |\mathbf{x}-\mathbf{y}|) \\ + 16\pi \rho V \langle a^2 \rangle \langle a \rangle \int_0^\infty dz \frac{\sin kz \cos kz}{k} g^{(2)}(z), \end{aligned} \quad (6)$$

where

$$\begin{aligned} \cos \gamma &= \mathbf{k} \cdot \mathbf{K} / kK, \\ \cos \theta &= \mathbf{x} \cdot \mathbf{y} / xy. \end{aligned}$$

The averages over the scattering lengths which appear in expression (6) may be written in terms of incoherent and coherent scattering lengths,  $a_{\text{inc}}$  and  $a_{\text{coh}}$ . The usual definitions are given by

$$\begin{aligned} a_{\text{inc}}^2 &= \langle a^2 \rangle - \langle a \rangle^2, \\ a_{\text{coh}}^2 &= \langle a \rangle^2. \end{aligned} \quad (7)$$

For the quantities which appear in expression (6) we then have

$$\begin{aligned} \langle a \rangle^3 &= a_{\text{coh}}^3 \\ \langle a^2 \rangle \langle a \rangle &= a_{\text{coh}}(a_{\text{inc}}^2 + a_{\text{coh}}^2). \end{aligned} \quad (8)$$

## DISCUSSION OF RESULTS

The above results are valid within the static approximation. In the case of neutron scattering this means that the validity is generally restricted to systems composed of heavy nuclei.<sup>4</sup> For x-ray scattering the static approximation is always valid owing to the smallness of the energy exchange compared to the energies of photons with wavelengths appropriate for diffraction experiments. In this case, one must replace the scattering lengths used above by appropriate atomic form factors.

Expression (6) provides the desired correction to the usual single scattering formula; it accounts for the interference between twice scattered neutrons and those which have suffered only one collision. The two terms appearing in (6) are analogous to those obtained in the single scattering case: The first is the "coherent" term and represents those events in which all scatters are from different nuclei [and hence it depends on  $g^{(3)}$ ], while the second is the "direct" term, in which the single-scattered neutron makes its collision with one of the nuclei encountered by the double-scattered neutron [hence it depends on  $g^{(2)}$  and is analogous to the incoherent term in the first Born approximation]. Expression (6) may be used to make multiple scattering corrections to experimental data if a reasonable guess

<sup>3</sup> T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).

<sup>4</sup> G. Placzek, *Phys. Rev.* **86**, 377 (1952).

at  $g^{(3)}$  can be made; it cannot, unfortunately, be used to measure the three-particle correlation function as an inverse Fourier transform cannot be taken.

A reasonable approximation to  $g^{(3)}$  might be Kirkwood's superposition approximation.<sup>3</sup> However, the limits on the integrals in (6) are such that they cannot be carried out in closed form even after this approximation is made so that a numerical calculation is necessary. Although calculations have not been performed, simple estimates of the integrals involved coupled with the fact that the incoherent scattering length is frequently larger than the coherent scattering length, lead us to believe that the second term generally dominates in expression (6). The assumption that multiple scattering is incoherent is the basis for other multiple-scattering corrections calculated using iterated applications of the single-scattering formula.<sup>5</sup>

<sup>5</sup> See, for example, G. H. Vineyard, *Phys. Rev.* **96**, 93 (1954); and S. Chandrasekhar, *Radiative Transfer* (Clarendon Press, Oxford, 1950).

It is possible to extend the above analysis to the non-static case by introducing time-dependent correlation functions. A simple calculation following the method of Van Hove<sup>2</sup> shows that this case can be treated by making the substitutions

$$\begin{aligned} g^{(2)}(\mathbf{r}) &\rightarrow G(\mathbf{r}, t), \\ g^{(3)}(\mathbf{r}, \mathbf{r}') &\rightarrow G(\mathbf{r}, \mathbf{r}', t, 0), \end{aligned}$$

where  $G(\mathbf{r}, t)$  is Van Hove's time-displaced two-particle correlation function and  $G(\mathbf{r}, \mathbf{r}', t, t')$  is the probability that given a particle at the origin at  $t=0$ , there be particles at  $\mathbf{r}$  and  $\mathbf{r}'$  (per unit volume at  $\mathbf{r}, \mathbf{r}'$ ) at times  $t$  and  $t'$ .

#### ACKNOWLEDGMENT

It is a pleasure to thank Professor F. Bloch, in conference with whom the subject of this paper was suggested.

### Analytic Wave Functions. IV. Inclusion of Correlation\*

R. G. BREENE, JR.†

*Space Science Laboratory, Missiles & Space Vehicles Department, General Electric Company, Philadelphia, Pennsylvania*

(Received May 3, 1962)

We have developed a general method for including correlation of the  $2p$  electrons in our atomic wave function programs. In introducing correlation, an appeal has been made to the interelectronic coordinate method of doing so. Tables are given which enable one to write down the  $2p$  correlated energy expression rapidly in terms of the radial integrals for any atoms having  $2p$  electrons of the same magnetic quantum number. One then solves for the correlation parameter  $a$ , and the result follows. In the case of an atom or atomic state we were treating for the first time, this entire procedure would take place after our programs had been applied to the obtention of the effective nuclear charges. Only the  $2p$  electrons have been considered by virtue of their importance to atomic interactions with exterior particles. We applied this to oxygen in its  $^3P$  ground state. We had previously obtained 2018.28 eV for the total energy. We now obtain 2039.81 eV. The experimental value is 2043.3.

#### I. INTRODUCTION

**I**N a series of papers<sup>1</sup> we have developed methods for machine computation of analytic atomic wave functions. Herein it is our purpose to develop a method of modifying these calculations so as to include the effects of electron correlation for the  $2p$  electrons in as facile a manner as possible. We confine ourselves to the  $2p$  electrons since we are most interested in the application of their results to exterior interaction.

The portions of the spatially-dependent interactions to which we shall pay particular attention are the

following: Two orbital electrons of opposite spin but the same  $n\ell m$  have precisely the same spatial wave functions. We may anticipate that, due to the Coulombic interaction between them, the orbital electrons demonstrate an affinity for opposite sides of the atom. The changes in energy which result from wave function changes aimed at describing such affinity are called correlation energy. We designate the modification of the wave functions as the inclusion of correlation.

Three principal methods of including correlation in the computation of atomic wave functions have been applied to date.<sup>2</sup> (1) In the first, it is supposed that the two electrons in the same  $n\ell m$  shell do not feel the same

† Consultant. 48 Maple Avenue, Centerville 59, Ohio.

\* Based on work performed under the auspices of the U. S. Air Force Ballistics Missiles Division.

<sup>1</sup> R. G. Breene, Jr., *Phys. Rev.* **111**, 1111 (1958); **113**, 809 (1959); **119**, 1615 (1960).

<sup>2</sup> J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II.