2016

Basis for Calculating Cross Sections for Nuclear Magnetic Resonance Spin-Modulated Polarized Neutron Scattering

Michael Kotlarchyk

George M. Thurston

This work is licensed under a [Creative Commons Attribution 4.0 License](https://creativecommons.org/licenses/by/4.0/).

Follow this and additional works at: <http://scholarworks.rit.edu/article>

Recommended Citation

Basis for calculating cross sections for nuclear magnetic resonance spin-modulated polarized neutron scattering. Kotlarchyk, Michael, & Thurston, George M. *Journal of Chemical Physics*. AIP Advances, Vol. 145, 244201, (2006). doi: 10.1063/1.4972994

This Article is brought to you for free and open access by RIT Scholar Works. It has been accepted for inclusion in Articles by an authorized administrator of RIT Scholar Works. For more information, please contact ritscholarworks@rit.edu.

Basis for calculating cross sections for nuclear magnetic resonance spin-modulated polarized neutron scattering

Michael Kotlarchyk and George M. Thurston

Citation: *J. Chem. Phys.* **145**, 244201 (2016); doi: 10.1063/1.4972994

View online: <http://dx.doi.org/10.1063/1.4972994>

View Table of Contents: <http://aip.scitation.org/toc/jcp/145/24>

Published by the [American Institute of Physics](#)

Basis for calculating cross sections for nuclear magnetic resonance spin-modulated polarized neutron scattering

Michael Kotlarchyk^{a)} and George M. Thurston^{b)}

School of Physics and Astronomy, Rochester Institute of Technology, Rochester, New York 14623, USA

(Received 29 September 2016; accepted 12 December 2016; published online 29 December 2016)

In this work we study the potential for utilizing the scattering of polarized neutrons from nuclei whose spin has been modulated using nuclear magnetic resonance (NMR). From first principles, we present an in-depth development of the differential scattering cross sections that would arise in such measurements from a hypothetical target system containing nuclei with non-zero spins. In particular, we investigate the modulation of the polarized scattering cross sections following the application of radio frequency pulses that impart initial transverse rotations to selected sets of spin-1/2 nuclei. The long-term aim is to provide a foundational treatment of the scattering cross section associated with enhancing scattering signals from selected nuclei using NMR techniques, thus employing minimal chemical or isotopic alterations, so as to advance the knowledge of macromolecular or liquid structure. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4972994>]

I. INTRODUCTION

In this work we continue the investigation of the potential for manipulating nuclear spins by nuclear magnetic resonance (NMR) techniques in order to enhance scattering of polarized neutrons from selected nuclei, a strategy that was proposed and described previously by Buckingham.¹ That work broadly considered the overall feasibility and utility of such experiments with a potential aim, for example, of studying slow structural changes such as those that occur in biological macromolecules. If scattering from NMR-selected nuclei can be robustly accomplished, it could serve as an extremely useful probe of soft-matter and other liquid systems. Our goal here is to develop a sound, foundational framework for calculating the neutron scattering cross sections associated with such experiments. Establishing these cross sections will be a basis for designing and evaluating experimental strategies to measure the desired signals, which are likely to be very small. The needed framework should be rigorous, yet flexible enough to address a variety of experimental strategies.

The present project was motivated by two pressing needs of very long standing. One is the need to create methods of more directly *measuring* the probabilistic, molecular orientation-dependent structure of liquids and liquid mixtures. Whereas standard techniques of small-angle X-ray (SAXS) and small-angle neutron scattering (SANS) have long been used to quantify liquid structure, the associated orientational information that can emerge, while certainly available, remains rather indirect. Knowing orientation-dependent liquid structure more quantitatively would facilitate the task of constructing sound statistical thermodynamic models for the liquid structure, free energy, chemical potentials, and other thermodynamic properties of importance in a broad variety of fields, ranging from chemical engineering to physiology.²⁻⁴

Particularly pressing realms in which orientation-dependent liquid structure is important include those of developing more understanding of the physics that produces the variety of effects that point mutations have on disease, such as cataract.⁵⁻⁸ Another motivating, pressing need is that of supplementing current methods to measure the structure of biological macromolecules, in order to help circumvent the bottleneck of crystallization and the limitations of NMR structural methods.

In a nutshell, the basic physical idea behind the present work is to find some way to use NMR to take advantage of the nuclear spin-dependent cross sections for neutron scattering. Simply put, can one “light up” the nuclei of one’s choice using some type of NMR spin preparation, and then use neutron scattering to see how far apart the selected nuclei are, while minimizing the signal from other nuclei? Could one ultimately even use neutron scattering to take advantage of the fact that different nuclei of the same type in the same molecule generally have slightly different Larmor frequencies, owing to their different chemical shifts?

From one point of view, the daunting and perhaps even discouraging aspect of trying to carry out such a task is the prospect of the tiny differences in neutron scattering signals that would be associated with the common, very small degrees of nuclear spin polarization. Current NMR preparation and signal-detection methods and equipment are exquisitely sensitive to signals associated with small degrees of nuclear polarization, but can small-angle neutron scattering *also* be made sensitive enough to be useful for the problems posed above at the outset? In Ref. 1, Buckingham has already provided order-of-magnitude estimates of the signal to be expected given the available neutron flux at that time. He gave an estimate that about a day of measurement time would be needed to achieve a signal-to-noise ratio of about 10, on a given detector out of an array of detectors, for the parameters used. That estimate made use of a typical degree of target proton polarization of 10^{-5} , at 300 K in a 600 MHz NMR magnet. Based on that estimate, the

^{a)}mnksps@rit.edu

^{b)}gmtsps@rit.edu

signal-to-noise obtainable in an NMR-modulated neutron scattering scenario may prove to be practically feasible. As pointed out by Buckingham, the signal-to-noise ratio should increase as the square-root of the incident neutron flux, and indeed, in the intervening years the fluxes available at various facilities worldwide have increased, with yet further improvements envisioned.

Many further considerations are needed to go beyond the order-of-magnitude signal-to-noise estimate given by Buckingham in order to evaluate the feasibility of specific sample environments, sample choices, beam and detector configurations, NMR preparation and neutron scattering protocols, and analysis methods. For example, NMR aspects affecting signal strength that are not considered in Ref. 1, nor in the present work, include density operator representations of selective preparation pulses, of relaxation considerations, and of the effects of spin coupling. The specifics associated with a chosen scenario will lead to a particular angular and temporal scattering signature that will call for appropriately tailored analysis protocols. Because the sensitivity considerations are intricate for each such choice, in this work our focus is on cross section considerations that are basic to large classes of design combinations.

In this spirit, the intended focus of the present work is to lay an essential part of the groundwork for making *quantitative* evaluations of the sensitivity of strategies proposed to achieve useful NMR-modulated, spin-polarized neutron scattering. By having suitable expressions, built from first principles, for the fundamental scattering cross sections for spin-polarized neutrons incident on an NMR-prepared sample, one can eventually be in a position to quantify the signal-to-noise ratio that would be expected from given, putative experimental designs.

In view of the extraordinary and growing variety and sophistication of useful NMR pulse sequences (e.g., Ref. 9), combined with conceivably time-resolved, inherently angle-dependent polarized SANS, here we can only scratch the surface of the possible types of NMR-modulated SANS experiments that could be envisioned. To get started assembling the needed elements from the quantum mechanical description of both the neutron scattering and the NMR, here we have made a relatively simple choice.

We now briefly describe related aspects of previous work (see also Ref. 1). Neutron scattering from polarized nuclei was first demonstrated in crystals.^{10–13} Hayter, Jenkin, and White¹⁴ detected a neutron scattering signal created using NMR pulses to flip nuclear polarization in crystals of lanthanum magnesium nitrate at low temperatures. They made use of the theoretical cross sections for the scattering of a polarized neutron beam from spin-polarized nuclei that were developed by Halpern and Johnson,¹⁵ Blume and Schermer,^{16–18} Moon,¹⁹ and other authors cited in Refs. 18 and 19. Scattering of neutrons from frozen biological and polymeric samples, spin-polarized at low temperatures, has been demonstrated and used for their study, for example, Refs. 20–23. Dynamic nuclear polarization^{24,25} (DNP) has also long been under investigation for its ability to polarize nuclei to enhance neutron scattering investigations.^{26–30} Some of these methods may be useful for enhancing cross sections to be calculated below, as pointed out in Ref. 1. However, DNP typically makes use of components

that are added to the system in order to provide for transferring polarization from electrons to nuclei. Here, in contrast to these works, our focus is on the possibility of scattering of spin-polarized neutrons from liquid, NMR spin-modulated samples that do not have added components.

In this work we provide a theoretical cross section formulation that is sufficiently general to encompass NMR preparation protocols that reflect the fact that the density operator of the spin or spin-plus-lattice system is a rigorous, natural, and customary quantum-mechanical description of NMR preparation and measurement pulse procedures.^{9,31–34} The cross sections calculated in our present work agree with those in Refs. 18 and 19 if magnetic contributions of electronic origin are not significant and if the target spin-density operator is diagonal, as is appropriate, for example, for computing thermal averages. The formulations in Ref. 18 as well as in more recent work³⁵ use a density operator to describe the state of the neutron beam but not that of the target. To emphasize, our focus is on the density operator of the *sample*, not that of the beam, and is most appropriate for use with well-polarized beams. It is important to note that while Refs. 18 and 19 do not use the density operator of the target system, they nevertheless treat the state of the sample in a form that is useful for the calculation of thermal averages and can also be adapted to some NMR pulse protocols, as demonstrated in Ref. 14.

II. STATIC SCATTERING CROSS SECTION AND SPIN-SPACE DECOUPLING APPROXIMATION

We begin with a useful form for the ensemble-average static cross section for the scattering of polarized neutrons from a spin-polarized target system,^{36,37}

$$\frac{d\sigma^{ss'}}{d\Omega}(\vec{Q}) = \left\langle \left\langle \sum_{ij} (\hat{b}_i^{ss'})^\dagger (\hat{b}_j^{ss'}) e^{-i\vec{Q}\cdot\vec{r}_i} e^{+i\vec{Q}\cdot\vec{r}_j} \right\rangle \right\rangle, \quad (1)$$

where $\vec{Q} = \vec{k} - \vec{k}'$ is the wavevector transfer between the initial neutron wavevector $\vec{k}$ and the final wavevector $\vec{k}'$, $\vec{r}_j$ denotes the position of target nucleus j , and $\hat{b}_j^{ss'}$ is the scattering-length operator for target nucleus j that connects the incident neutron spin state s with the final neutron spin state s' . In Eq. (1), we have denoted the ensemble average by double brackets ($\langle\langle \dots \rangle\rangle$) to emphasize the fact that it is an average over *both* the spins and the positions of the nuclei.

Denoting the polarization-state of the neutron $|s\rangle$ by either $|+\rangle$, for spin up, or by $|-\rangle$, for spin down, the scattering length operators for the j th nucleus can be written in terms of its z -component, raising, and lowering angular momentum operators $\hat{I}_z$, $\hat{I}_+$, and $\hat{I}_-$, respectively, as follows:³⁶

$$\begin{aligned} \hat{b}_j^{++} &= (A + B\hat{I}_z)_j; & \hat{b}_j^{--} &= (A - B\hat{I}_z)_j; \\ \hat{b}_j^{+-} &= (B\hat{I}_+)_j; & \hat{b}_j^{-+} &= (B\hat{I}_-)_j, \end{aligned} \quad (2)$$

in which, for any one particular target nucleus, the constants A and B can be expressed in terms of the two scalar scattering lengths b^+ and b^- , which correspond to the cases where the total spin quantum numbers, t , of the neutron-nucleus system

are $t_+ = I + \frac{1}{2}$ and $t_- = I - \frac{1}{2}$, respectively. Specifically,

$$A_j = \frac{(I_j + 1)b_j^+ + I_j b_j^-}{2I_j + 1} \quad \text{and} \quad B_j = \frac{b_j^+ - b_j^-}{2I_j + 1}, \quad (3)$$

in which I_j is the total spin quantum number for nucleus j . The utility of the expressions in Eqs. (2) and (3) stems from the fact that b^+ and b^- values have been determined experimentally and tabulated for various nuclei.^{36,37}

In the following we develop the cross section given by Eq. (1) when the spin states of the nuclei respond to an applied magnetic field, to various NMR pulses, and to other factors that affect their degree of polarization. For simplicity in the present treatment we assume that the responses of different nuclei to the imposed external fields are independent of one another. Technically, as will be developed below, this is equivalent to assuming that the density operators for the nuclear spin states factor into products of density operators for each nucleus and that the nuclear spin states are uncorrelated with their *relative* positions. However, it is important to note that spin states of different nuclei can nevertheless be closely related to one another, owing to their commonality of response to applied fields and other sample conditions.

By making the decoupling approximations just described, for the time being we postpone the more complicated description of polarized neutron scattering that will be needed when nuclear spins are linked by one or a few covalent bonds by scalar, or J -coupling, and when nuclear spins are directly coupled by through-space spin-spin interactions. Also, as discussed below, for the present purpose we neglect the coupling with the surroundings (“lattice”) that will lead to longitudinal and transverse relaxation of the nuclear spin polarizations. Due in part to the spatial proximity needed for the coupling effects, the associated spin and position variables have correlations that the present analysis does not consider.

In the context of our present neglect of scalar and direct spin-spin coupling, it should be kept in mind that the Fourier transform of scattering length correlations provided by SANS can respond to spatial correlations ranging from those at interatomic scales to those at distances very large compared with even large biological macromolecules. Because these accessible SANS distance scales greatly exceed those needed for nuclear spin-spin coupling, there remains a large realm of spatial separations to which the present analysis will apply, despite the neglect of scalar and direct coupling.

In regard to the present neglect of longitudinal and transverse relaxation processes, we anticipate that their ultimate essential effect will be to replace the signal strengths presented below by appropriate time-average integrals. These time-averages and their associated durations will be critical for designing effective preparation and measurement cycle timing and strategy. While the prototypical calculation presented here will need to be considerably altered to reflect the more elaborate nature of the density matrix, its basic nature and magnitude will nevertheless remain fundamentally relevant.

Consistent with the present decoupling approximation, we rewrite Eq. (1) to distinguish between the spin average, denoted by an overline ($\overline{\dots}$) and the spatial average, denoted by $\langle \dots \rangle$,

$$\frac{d\sigma^{ss'}}{d\Omega}(\vec{Q}) = \left\langle \sum_{ij} \overline{\left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right)} e^{+i\vec{Q} \cdot (\vec{r}_j - \vec{r}_i)} \right\rangle. \quad (4)$$

At this point, it is interesting to note that each of the indices i and j enters into *both* the spin *and* the spatial averages that appear in Eq. (4). As a consequence, despite the assumption that the spin states of different nuclei are independent of their relative positions, the results of evaluating the spin averages of the cross sections, for various types of polarized neutron scattering from an NMR-modulated sample, can in principle lead to methods of gaining information about the relative positions $\vec{r}_{ji} = \vec{r}_j - \vec{r}_i$ of NMR-selected nuclei.¹

We now consider further the spin-averaged scattering-length product that appears in Eq. (4). This can be expressed in terms of the joint spin-state density-operator for spins i and j , $\hat{\rho}_{ij,\text{spin}}$,

$$\overline{\left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right)} = \text{Tr} \left[\hat{\rho}_{ij,\text{spin}} \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right) \right]. \quad (5)$$

Again consistent with our present neglect of J and direct coupling, we assume, for different nuclei, that the joint spin-state density-operator can be written as a product of spin-density operators for spins i and j : $\hat{\rho}_{ij,\text{spin}} = \hat{\rho}_{i,\text{spin}} \hat{\rho}_{j,\text{spin}}$, in which $\hat{\rho}_{i,\text{spin}}$ is the single-nucleus density matrix for nucleus i and has the property $\text{Tr}[\hat{\rho}_{i,\text{spin}}] = 1$. On the other hand, if $i = j$, we have $\hat{\rho}_{ij,\text{spin}} = \hat{\rho}_{i,\text{spin}}$. Equivalently, $\hat{\rho}_{ij,\text{spin}} = (\hat{\rho}_{i,\text{spin}} - \hat{\rho}_{i,\text{spin}} \hat{\rho}_{j,\text{spin}}) \delta_{ij} + \hat{\rho}_{i,\text{spin}} \hat{\rho}_{j,\text{spin}}$. Consequently,

$$\begin{aligned} \overline{\left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right)} &= \text{Tr} \left[\hat{\rho}_i \hat{\rho}_j \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right) \right] \\ &= \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j \left(\hat{b}_j^{ss'} \right) \right] \quad (i \neq j) \\ &= \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_i^{ss'} \right) \right] \quad (i = j), \end{aligned} \quad (6)$$

in which we have omitted the “spin” designation from the density operators for clarity, and in which $\text{Tr}_{(i)}$ represents a “reduced” trace over the spin states for nucleus i alone. The two cases can be written together as

$$\begin{aligned} \overline{\left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right)} &= \left\{ \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_i^{ss'} \right) \right] \right. \\ &\quad - \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j \left(\hat{b}_j^{ss'} \right) \right] \} \delta_{ij} \\ &\quad + \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j \left(\hat{b}_j^{ss'} \right) \right]. \end{aligned} \quad (7)$$

However, because terms for which $i = j$ are the only ones that contribute to the portion in curly brackets, we can replace j by i in that term to obtain

$$\begin{aligned} \overline{\left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_j^{ss'} \right)} &= \left\{ \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_i^{ss'} \right) \right] \right. \\ &\quad - \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right) \right] \} \delta_{ij} \\ &\quad + \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j \left(\hat{b}_j^{ss'} \right) \right]. \end{aligned} \quad (8)$$

We now define coherent and incoherent cross sections as follows:

$$\left(b_{ij}^{ss'} \right)_{\text{coh}}^2 = \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j \left(\hat{b}_j^{ss'} \right) \right], \quad (9)$$

$$\begin{aligned} \left(b_i^{ss'} \right)_{\text{inc}}^2 &= \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \left(\hat{b}_i^{ss'} \right) \right] \\ &\quad - \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right)^\dagger \right] \text{Tr}_{(i)} \left[\hat{\rho}_i \left(\hat{b}_i^{ss'} \right) \right], \end{aligned} \quad (10)$$

in terms of which

$$\overline{(\hat{b}_i^{ss'})^\dagger (\hat{b}_j^{ss'})} = (b_i^{ss'})_{\text{inc}}^2 \delta_{ij} + (b_{ij}^{ss'})_{\text{coh}}^2. \quad (11)$$

Inserting Eq. (11) into Eq. (4) puts the differential scattering cross section in the form

$$\frac{d\sigma^{ss'}}{d\Omega}(\vec{Q}) = \left(\frac{k'}{k}\right) \left[(b_{\text{inc}}^{ss'})^2 + \left\langle \sum_{ij} (b_{ij}^{ss'})_{\text{coh}}^2 e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle \right], \quad (12)$$

in which $\vec{r}_{ji} = \vec{r}_j - \vec{r}_i$ and $(b_{\text{inc}}^{ss'})^2 = \sum_i (b_i^{ss'})_{\text{inc}}^2$. Eq. (12), in combination with the expressions in Eqs. (2), (3), (9), and (10), allows for calculation of both the $\vec{Q}$ -independent incoherent cross section and the coherent polarized neutron scattering cross section from a spin-polarized target, all within the present spin-space decoupling approximation. In the calculations below, for clarity we now use the elastic scattering consequence $k' = k$ in elaborating specific instances of Eq. (12).

III. SPIN-DENSITY OPERATOR FOR A PROTOTYPICAL NMR-SANS EXPERIMENT

We now use Eq. (12) to calculate the cross sections resulting from a prototypical, candidate NMR spin-modulation scenario. This requires a model of the spin-density operators of the system needed to evaluate Eqs. (9) and (10). In the present work we restrict our analysis of the static cross section to density operators that are independent of time, which, nevertheless, we will need to have evolved forward in time starting from an equilibrium or other steady-state situation. To this end, we consider a single spin-1/2 nucleus that initially has probabilities p_+ and p_- of being spin-up and spin-down, respectively, along the positive z -axis ($p_+ + p_- = 1$), to which an NMR pulse will subsequently be applied.

The following derivation of the density operator needed to evaluate Eq. (12), for our choice of a prototype NMR preparation scenario, follows a standard pattern in the study of NMR, and its physical basis is well-described in a number of books, for example, Refs. 9, 31–34, and 37. Nevertheless, we include the details relevant to the present case, in part because we hope that the present work can be readily followed by investigators in each of the fields of nuclear magnetic resonance and small-angle neutron scattering, who may be less familiar with the other field. By doing so we also set notation for subsequent analysis of possibly useful experimental protocols that emerge from the resulting cross sections and establish a starting point for analysis of more sophisticated NMR preparation schemes as well as effects whose analysis we postpone here.

We take the density operator at time $t = 0$ to be

$$\begin{aligned} \hat{\rho}(0) &= \begin{pmatrix} p_+ & 0 \\ 0 & p_- \end{pmatrix} = \begin{pmatrix} p_+ & 0 \\ 0 & (1 - p_+) \end{pmatrix} \\ &= \frac{1}{2} \hat{\mathbb{I}} + P \left(\frac{1}{2} \right) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2} \hat{\mathbb{I}} + P \hat{I}_z, \end{aligned} \quad (13)$$

where $\hat{\mathbb{I}}$ is the identity operator and $P = (+1)p_+ + (-1)p_- = 2p_+ - 1$ is the polarization state of the target nucleus ($-1 \leq P \leq +1$). This form of $\hat{\rho}$, where the off-diagonal elements are zero, is applicable if the phases of the quantum-mechanical spin states of the target nuclei are randomly distributed. That is to say, the density matrix of the target system

does not exhibit any coherence (definite phase relationship) between the up and down spin states. For example, this form would hold for a statistical mixture of up and down states in thermal equilibrium. We note at the outset that while the polarization may be set by conditions of thermal equilibrium, in which case the polarization is typically quite small at normal temperatures, there exist techniques by which P can be significantly increased; see, for example, Refs. 25 and 38–40. It may then become necessary to incorporate non-zero off-diagonal elements into the initial density operator.

We now find the single-nucleus density operator $\hat{\rho}_i$ immediately *after* a radio-frequency (RF) pulse that is applied to a nucleus that is initially in polarization state P_i , as described by the density operator in Eq. (13).

During the pulse, the total applied magnetic field is

$$\mathbf{H}(t) = H_0 \mathbf{e}_z + H_{\text{RF}} [\mathbf{e}_x \cos(\omega t + \phi) - \mathbf{e}_y \sin(\omega t + \phi)]. \quad (14)$$

The negative sign in front of $\mathbf{e}_y$ makes the sense of rotation of the RF field the same as the sense of the Larmor precession about the z -axis due to the longitudinal field. Eq. (13) gives the $t = 0$ density matrix as viewed in the laboratory reference frame. However^{31,37} at any time t , one can transform between the density matrix $\hat{\rho}$ in the lab frame to a density matrix $\hat{\rho}_R$ viewed from a frame that rotates at the RF ω according to

$$\hat{\rho}_R = \hat{R}^{-1} \hat{\rho} \hat{R} \quad (15)$$

or

$$\hat{\rho} = \hat{R} \hat{\rho}_R \hat{R}^{-1}, \quad (16)$$

where the operator

$$\hat{R} = \exp[i(\omega t + \phi) \hat{I}_z] \quad (17)$$

produces a rotation of angle $\omega t + \phi$ about the z -axis. But at $t = 0$, $\hat{R}$ and $\hat{\rho}(0)$ commute, so we have $\hat{\rho}_R(0) = \hat{\rho}(0)$.

In the lab frame, the density matrix at time t is obtained by solving the equation of motion

$$\frac{d\hat{\rho}}{dt} = \frac{i}{\hbar} [\hat{\rho}, \hat{\mathcal{H}}] \quad (18)$$

governed by the time-dependent lab-frame interaction Hamiltonian

$$\hat{\mathcal{H}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{H}(t), \quad (19)$$

where $\hat{\boldsymbol{\mu}} = \gamma \hbar \mathbf{I}$ is the magnetic-moment operator for a nucleus with spin $\mathbf{I}$. γ is the gyromagnetic ratio of the nucleus. The lab Hamiltonian is then

$$\hat{\mathcal{H}} = -\gamma \hbar H_0 \hat{I}_z - \gamma \hbar H_{\text{RF}} [\hat{I}_x \cos(\omega t + \phi) - \hat{I}_y \sin(\omega t + \phi)]. \quad (20)$$

For clarity in this section, in the Hamiltonian we regard the symbols H_0 and H_{RF} as standing for the *shielded* magnetic fields at the nucleus, $H_0(1 - \sigma_j)$ and $H_{\text{RF}}(1 - \sigma_j)$, where σ_j stands for the orientationally averaged chemical shift of nucleus j ; thus, we assume that the sample is in the liquid state. For clarity we also set the phases $\phi = 0$ in the developments below; these can readily be put back as the need arises.

Eq. (20) can be transformed to (see, e.g., Ref. 37, Section 10.4)

$$\hat{\mathcal{H}} = -\gamma \hbar H_0 \hat{I}_z - \gamma \hbar H_{\text{RF}} \hat{R} \hat{I}_x \hat{R}^{-1}. \quad (21)$$

Combining Eqs. (15), (16), (18), and (21), one finds the equation of motion for the density matrix in the rotating frame to have the same form as that given in the lab frame but governed by an effective Hamiltonian $\hat{\mathcal{H}}_{\text{eff}}$ that is independent of time, i.e.,

$$\frac{d\hat{\rho}_R}{dt} = \frac{i}{\hbar} [\hat{\rho}_R, \hat{\mathcal{H}}_{\text{eff}}], \quad (22)$$

with

$$\hat{\mathcal{H}}_{\text{eff}} = -\gamma\hbar h_0 \hat{I}_z - \gamma\hbar H_{\text{RF}} \hat{I}_x, \quad (23)$$

where we have used the definition

$$h_0 = \left(H_0 - \frac{\omega}{\gamma} \right). \quad (24)$$

Observe that when the RF ω matches the Larmor precession frequency given by $\omega_0 = \gamma H_0$, then h_0 vanishes and $\hat{\mathcal{H}}_{\text{eff}} = -\gamma\hbar H_{\text{RF}} \hat{I}_x$, i.e., when the RF is at resonance with the Larmor frequency, the effective Hamiltonian in the rotating frame looks exactly like a lab Hamiltonian in a static field H_{RF} directed along the x -axis. Consequently, from the vantage point of the rotating frame, the spin-state will “precess,” or flip about the x -axis at frequency $\omega_{\text{flip}} = \gamma H_{\text{RF}}$. In other words, one introduces a “ θ_x -pulse” (rotating the spin-state by angle θ_x away from the z -axis) by applying an RF pulse of duration $t = \theta_x / \omega_{\text{flip}} = \theta_x / \gamma H_{\text{RF}}$. If the RF is off-resonance, a transverse precession will also occur in the rotating frame at frequency $|\omega - \omega_0|$.

We will now work in the rotating reference frame, with the understanding that we will ultimately transform back to the laboratory frame in order to use the appropriate density matrix for calculating the corresponding polarized neutron scattering cross sections in Eqs. (9) and (10). Let the duration of the RF pulse be t_p . Because the effective Hamiltonian in the rotating frame is time-independent, one can evolve the density matrix forward from time $t = 0$ to the end of the pulse at time $t = t_p$ according to

$$\hat{\rho}_R(t_p) = e^{-i\hat{\mathcal{H}}_{\text{eff}} t_p / \hbar} \hat{\rho}_R(0) e^{+i\hat{\mathcal{H}}_{\text{eff}} t_p / \hbar}. \quad (25)$$

Because the RF is assumed to be close to resonance, during the time the pulse is on, we have $H_{\text{RF}} \gg h_0$, so we approximate the Hamiltonian as

$$\hat{\mathcal{H}}_{\text{eff}}^{(\text{on})} = -\gamma\hbar H_{\text{RF}} \hat{I}_x. \quad (26)$$

The rotating-frame density matrix at the end of the pulse is then given by

$$\begin{aligned} \hat{\rho}_R(t_p) &= e^{-i\hat{\mathcal{H}}_{\text{eff}}^{(\text{on})} t_p / \hbar} \left(\frac{1}{2} \hat{\mathbb{1}} + P \hat{I}_z \right) e^{+i\hat{\mathcal{H}}_{\text{eff}}^{(\text{on})} t_p / \hbar} \\ &= \frac{1}{2} \hat{\mathbb{1}} + P e^{+i\omega_{\text{flip}} t_p} \hat{I}_x e^{-i\omega_{\text{flip}} t_p} \hat{I}_x \\ &= \frac{1}{2} \hat{\mathbb{1}} + P e^{+i\theta_x} \hat{I}_x e^{-i\theta_x} \hat{I}_x. \end{aligned} \quad (27)$$

Again using Ref. 37, Section 10.4, this can be rewritten as

$$\hat{\rho}_R(t_p) = \frac{1}{2} \hat{\mathbb{1}} + P (\hat{I}_y \sin \theta_x + \hat{I}_z \cos \theta_x), \quad (28)$$

i.e., the operator sequence in the second term of the last line of Eq. (27) corresponds to a rotation about the x -axis.

Transforming back to the laboratory frame with use of Eq. (16), the density operator at the end of the pulse is

$$\begin{aligned} \hat{\rho}_i &= \frac{1}{2} \hat{\mathbb{1}}_i + P_i \sin \theta_i \left[(\hat{I}_x)_i \sin(\omega t_p) + (\hat{I}_y)_i \cos(\omega t_p) \right] \\ &\quad + P_i \cos \theta_i (\hat{I}_z)_i, \end{aligned} \quad (29)$$

in which we have inserted the subscript “ i ” to refer to the i th nucleus. In terms of the raising and lowering operators for nucleus i , and using $\omega t_p = (\omega / (\omega_{\text{flip}})_i) \theta_i$, Eq. (29) can be rewritten in the form

$$\begin{aligned} \hat{\rho}_i &= \frac{1}{2} \hat{\mathbb{1}}_i + \frac{i}{2} P_i \sin \theta_i \left[e^{-i(\omega / (\omega_{\text{flip}})_i) \theta_i} (\hat{I}_-)_i - e^{+i(\omega / (\omega_{\text{flip}})_i) \theta_i} (\hat{I}_+)_i \right] \\ &\quad + P_i \cos \theta_i (\hat{I}_z)_i. \end{aligned} \quad (30)$$

The resulting density operator $\hat{\rho}_i$ is Hermitian and has trace 1, as it must. Use of the raising and lowering operators, as in Eq. (30), greatly simplifies the evaluation of the traces over spin states needed to evaluate the scattering cross sections in Eqs. (9) and (10).

IV. POLARIZED NEUTRON SCATTERING CROSS SECTIONS FOR A PROTOTYPICAL NMR-SANS EXPERIMENT

We now envision a hypothetical scenario, depicted schematically in Fig. 1, in which a collection of nuclei has been prepared with NMR so that it is well-modeled by the spin density operator given in Eq. (30). The sample is then quickly removed from the magnetic field H_0 , and polarized neutron scattering is performed during the time interval within which the selected nuclei in the sample remain sufficiently polarized. The sample is then returned to the NMR apparatus, and the cycle is repeated. As mentioned above, we postpone quantitative consideration of the relaxation effects that will affect the evolution of the density operator subsequent to times when Eq. (30) is a good model.

We now use Eq. (30) to calculate the neutron scattering cross sections for the various cases of incident neutron spin ($s = \pm$) and detected neutron-spin ($s' = \pm$). By keeping the subscript i on the density operator for each of the distinct target nuclei, including on the initial rotation angle θ_i , we retain the ability of the formalism to model distinct scattering cross sections that correspond to nuclei of different chemical elements, or to nuclei that have differing chemical shifts, or that have undergone distinct NMR preparations.

For $s = +$ and $s' = +$, or the $(++)$ -case, from Eqs. (2), (9), and (10), we need to evaluate

$$\text{Tr}_{(j)} \left[\hat{\rho}_j (\hat{b}_j^{++}) \right] = \text{Tr}_{(j)} \left[\hat{\rho}_j (A_j + B_j (\hat{I}_z)_j) \right]. \quad (31)$$

For evaluating the traces found here and later, observe that

$$\begin{aligned} I_+ |\beta\rangle &= |\alpha\rangle, & I_- |\alpha\rangle &= |\beta\rangle, \\ I_+ |\alpha\rangle &= 0, & I_- |\beta\rangle &= 0, \\ I_z |\alpha\rangle &= \frac{1}{2} |\alpha\rangle, & I_z |\beta\rangle &= -\frac{1}{2} |\beta\rangle. \end{aligned} \quad (32)$$

Upon inserting the expression for $\hat{\rho}_j$ from Eq. (30) into Eq. (31), note first that the parts of the trace corresponding to the cross terms involving the complex exponentials both vanish because they multiply the raising and lowering operators.

FIG. 1. A possible measurement scenario; see text.

Of the remaining terms in the trace, those that are independent of the polarization P_j are

$$\text{Tr}_{(j)} \left[\frac{1}{2} A_j \hat{I}_j + \frac{1}{2} B_j \hat{I}_j (\hat{I}_z)_j \right] = \frac{1}{2} A_j \text{Tr}_{(j)} [\hat{I}_j] = A_j, \quad (33)$$

in which we have used $\text{Tr}_{(j)} [\hat{I}_j] = 2$ and $\text{Tr}_{(j)} [\hat{I}_z] = 0$. The terms that involve P_j are

$$\begin{aligned} \text{Tr}_{(j)} [P_j \cos \theta_j (\hat{I}_z)_j (A_j + B_j (\hat{I}_z)_j)] &= B_j P_j \cos \theta_j \text{Tr}_{(j)} [\hat{I}_z^2] \\ &= \frac{1}{2} B_j P_j \cos \theta_j, \end{aligned} \quad (34)$$

in which we have again used $\text{Tr}_{(j)} [\hat{I}_z] = 0$, together with $\text{Tr}_{(j)} [\hat{I}_z^2] = \frac{1}{2}$. Combining Eqs. (31), (33), and (34), we have

$$\text{Tr}_{(j)} [\hat{\rho}_j \hat{b}_j^{++}] = A_j + \frac{1}{2} B_j P_j \cos \theta_j. \quad (35)$$

Similarly, because $(\hat{b}_i^{++})^\dagger = (\hat{b}_i^{++}) = A_i + B_i (\hat{I}_z)_i$, we have

$$\text{Tr}_{(i)} [\hat{\rho}_i (\hat{b}_i^{++})^\dagger] = A_i + \frac{1}{2} B_i P_i \cos \theta_i. \quad (36)$$

For the incoherent cross section in Eq. (10), we also need

$$\begin{aligned} \text{Tr}_{(i)} [\hat{\rho}_i (\hat{b}_i^{++})^\dagger (\hat{b}_i^{++})] &= \text{Tr}_{(i)} [\hat{\rho}_i (A_i + B_i (\hat{I}_z)_i) (A_i + B_i (\hat{I}_z)_i)] \\ &= \text{Tr}_{(i)} \left[\left(\frac{1}{2} \hat{I}_i + P_i \cos \theta_i (\hat{I}_z)_i \right) \right. \\ &\quad \times (A_i + B_i (\hat{I}_z)_i) (A_i + B_i (\hat{I}_z)_i) \left. \right], \end{aligned} \quad (37)$$

in the last line of which we first used Eq. (30) for $\hat{\rho}_i$ and then used $\text{Tr}_{(i)} [(\hat{I}_\pm)_i (\hat{I}_z)_i^k] = 0$ for $k = 0, 1, 2$. The trace of the terms on the right-hand side of Eq. (37) that are independent of polarization P_i is $A_i^2 + \frac{1}{4} B_i^2$. In the case of the terms that depend on P_i , only the two terms that involve $\text{Tr}_{(i)} [\hat{I}_z^2] = \frac{1}{2}$ contribute because $\text{Tr}_{(i)} [\hat{I}_z^3] = 0$ and $\text{Tr}_{(i)} [(\hat{I}_z)_i] = 0$. Therefore the P_i -dependent terms give a contribution $A_i B_i P_i \cos \theta_i$ to the trace, and altogether

$$\text{Tr}_{(i)} [\hat{\rho}_i (\hat{b}_i^{++})^\dagger (\hat{b}_i^{++})] = A_i^2 + \frac{1}{4} B_i^2 + A_i B_i P_i \cos \theta_i. \quad (38)$$

We now assemble the results above. First, with the use of Eqs. (9), (35), and (36) we have

$$(b_{ij}^{++})_{\text{coh}}^2 = \left(A_i + \frac{1}{2} B_i P_i \cos \theta_i \right) \left(A_j + \frac{1}{2} B_j P_j \cos \theta_j \right), \quad (39)$$

while with use of Eqs. (10) and (38), in addition to (35) and (36), we have

$$\begin{aligned} (b_i^{++})_{\text{inc}}^2 &= A_i^2 + \frac{1}{4} B_i^2 + A_i B_i P_i \cos \theta_i \\ &\quad - \left(A_i + \frac{1}{2} B_i P_i \cos \theta_i \right) \left(A_i + \frac{1}{2} B_i P_i \cos \theta_i \right) \\ &= \frac{1}{4} B_i^2 (1 - P_i^2 \cos^2 \theta_i). \end{aligned} \quad (40)$$

Inserting Eqs. (39) and (40) into Eq. (12), we obtain the $(++)$ cross section in the form

$$\begin{aligned} \frac{d\sigma^{++}}{d\Omega}(\vec{Q}) &= \frac{1}{4} \sum_i B_i^2 (1 - P_i^2 \cos^2 \theta_i) + \left\langle \sum_{ij} \left(A_i + \frac{1}{2} B_i P_i \cos \theta_i \right) \right. \\ &\quad \times \left. \left(A_j + \frac{1}{2} B_j P_j \cos \theta_j \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \end{aligned} \quad (41)$$

Because of the similar forms of the respective scattering length operators (Eq. (2)), the $(--)$ cross section can be obtained by replacing B_i in the $(++)$ cross section of Eq. (41) with $-B_i$, giving

$$\begin{aligned} \frac{d\sigma^{--}}{d\Omega}(\vec{Q}) &= \frac{1}{4} \sum_i B_i^2 (1 - P_i^2 \cos^2 \theta_i) + \left\langle \sum_{ij} \left(A_i - \frac{1}{2} B_i P_i \cos \theta_i \right) \right. \\ &\quad \times \left. \left(A_j - \frac{1}{2} B_j P_j \cos \theta_j \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \end{aligned} \quad (42)$$

Note that Eqs. (41) and (42) show that if a $(++)$ cross section were to be measured with a set of NMR rotation preparation angles $\{\theta_i\}$, it would have the same value as a $(--)$ cross section prepared so that each θ_i is replaced by its supplement, $\pi - \theta_i$,

$$\frac{d\sigma^{++}}{d\Omega}(\vec{Q})[\text{for } \{\theta_i\}] = \frac{d\sigma^{--}}{d\Omega}(\vec{Q})[\text{for } \{\pi - \theta_i\}]. \quad (43)$$

We now compare Eqs. (39)–(41) with the corresponding scattering length and governing cross sections given in

Eqs. (2) and (4) of Ref. 1, respectively. The analysis in Ref. 1 focused on polarized neutron scattering from a sample that was taken to be subject to a square-wave pattern of NMR π -pulses. Using the present notation, and putting relaxation and other ancillary considerations discussed in Ref. 1 to the side, such a square-wave pattern would produce an alternation between $\theta_i = \pi$ and $\theta_i = 0$. In Eq. (2) and the text following Eq. (2) in Ref. 1, the effective scattering length, called $b_{\text{effective}}$ there, is given for neutrons in a polarized beam, subjected to π -pulses, as $b_{\text{effective}} = (1/4)(3b^+ + b^-) \pm (b^+ - b^-)P/4$. With use of the present Eq. (2), we thus have $b_{\text{effective}} = A \pm (1/2)BP$. Thus, specializing to the values $\cos \theta_i = \pm 1$ relevant for this comparison, $b_{\text{effective}}$ in Ref. 1 agrees with each of the two factors of the form $A_i + \frac{1}{2}B_iP_i \cos \theta_i$ that appear on the right-hand side of the present Eq. (39).

For each pair of nuclei of types labeled by α and β in Ref. 1, the product $b_\alpha b_\beta$ of the appropriate $b_{\text{effective}}$ values then enters into the second sum of Eq. (4) of Ref. 1, which contains the Q -dependent part of the polarized cross sections. For convenience we quote Eq. (4) of Ref. 1 here,

$$I(Q) \propto \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + \sum_{\alpha\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} [S_{\alpha\beta}(Q) - 1], \quad (44)$$

in which $I(Q)$ denotes the intensity of elastic scattering of polarized neutrons at wave vector magnitude Q , c_{α} is the mole fraction of the nucleus α whose scattering length is b_{α} , and $S_{\alpha\beta}(Q)$ is the partial structure factor.

Owing to the equality just established (for $\theta = 0$ or π) between the present $(b_{ij}^{++})_{\text{coh}}^2$ and the corresponding product $b_{\text{effective}}(i)b_{\text{effective}}(j)$ of Ref. 1 (which appears as $b_{\alpha}b_{\beta}$ in Eq. (44)), this coherent contribution is consistent with the present use of $(b_{ij}^{++})_{\text{coh}}^2$ in the Q -dependent part of the scattering cross section given in Eq. (41) and, similarly, Eq. (42).

However, the incoherent cross sections given by Eqs. (41) and (42), owing to the result for $(b_i^{++})_{\text{inc}}^2$ in Eq. (40), differ from that appearing in Eq. (44). Specifically, by comparing the present Eqs. (39) and (40), it is apparent that in general, $(b_i^{++})_{\text{inc}}^2 \neq (b_{ii}^{++})_{\text{coh}}^2$. This differs from the use in Eq. (44) of b_{α}^2 as the contribution of nucleus α to the incoherent portion of the scattering cross section.

As a further consequence, the present Eqs. (41) and (42) each predict that upon taking the difference between $\theta = 0$ and $\theta = \pi$ pulse ($++$) (or $--$) cross sections, the incoherent portions would cancel with one another. In contrast, according to Eq. (44), upon taking the same difference, each nucleus would instead contribute $b_{\text{effective}}(i)[\theta_i=0]^2 - b_{\text{effective}}(i)[\theta_i=\pi]^2 = (A + (1/2)BP)^2 - (A - (1/2)BP)^2 = 2ABP$ to the incoherent cross section.

As an important check, we note that Eqs. (41) and (42) reduce correctly to the cross sections for neutron scattering from an unpolarized target by setting the polarizations P_i , which are normally very small, to 0. In that case, one has

$$\begin{aligned} (b_{ij}^{++})_{\text{coh}}^2 &= (b_{ij}^{--})_{\text{coh}}^2 = A_i A_j \quad (\text{for } P_i = P_j = 0), \\ (b_i^{++})_{\text{inc}}^2 &= (b_i^{--})_{\text{inc}}^2 = \frac{1}{4} B_i^2 \quad (\text{for } P_i = P_j = 0) \end{aligned} \quad (45)$$

giving

$$\frac{d\sigma^{++}}{d\Omega}(\vec{Q}) = \frac{d\sigma^{--}}{d\Omega}(\vec{Q}) = \frac{1}{4} \sum_i B_i^2 + \left\langle \sum_{ij} A_i A_j e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \quad (46)$$

For N unpolarized target nuclei of a single spin- $\frac{1}{2}$ species, Eq. (46) reduces further to the expected result for the no spin-flip case for scattering from an unpolarized target,^{3,36,37}

$$\begin{aligned} \frac{d\sigma^{++}}{d\Omega}(\vec{Q}) &= \frac{d\sigma^{--}}{d\Omega}(\vec{Q}) = \frac{1}{3} N b_{\text{inc}}^2 + \left\langle \sum_{ij} A^2 e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle \\ &= \frac{1}{3} N b_{\text{inc}}^2 + N A^2 \left\langle \frac{1}{N} \sum_{ij} e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle \\ &= \frac{1}{3} N b_{\text{inc}}^2 + N A^2 S(\vec{Q}), \end{aligned} \quad (47)$$

in which $S(\vec{Q})$ is the static structure factor, and in which we have used the definition³⁷

$$b_{\text{inc}}^2 = I(I+1)B^2 = \frac{3}{4}B^2. \quad (48)$$

We now compute the corresponding neutron spin-flip scattering cross sections. For the $(+-)$ case,

$$\begin{aligned} \text{Tr}_{(j)} \{ \hat{\rho}_j (\hat{b}_j^{+-}) \} &= \text{Tr}_{(j)} \{ \hat{\rho}_j (B_j \hat{I}_+)_j \} \\ &= B_j \text{Tr}_{(j)} \{ \hat{\rho}_j (\hat{I}_+)_j \} \\ &= B_j \text{Tr}_{(j)} \left\{ \frac{1}{2} (\hat{I}_+)_j + P_j \cos \theta_j (\hat{I}_z)_j (\hat{I}_+)_j \right. \\ &\quad \left. + \frac{1}{2} i P_j \sin \theta_j e^{-i(\omega t_1)} (\hat{I}_-)_j (\hat{I}_+)_j \right. \\ &\quad \left. - \frac{1}{2} i P_j \sin \theta_j e^{+i(\omega t_1)} (\hat{I}_+)_j (\hat{I}_-)_j \right\}. \end{aligned} \quad (49)$$

In addition to the traces previously considered, also observe that

$$\begin{aligned} \text{Tr}_{(j)} \left[(\hat{I}_-)_j (\hat{I}_+)_j \right] &= \langle \alpha | I_- I_+ | \alpha \rangle + \langle \beta | I_- I_+ | \beta \rangle = 1, \\ \text{Tr}_{(j)} \left[(\hat{I}_+)_j (\hat{I}_+)_j \right] &= \langle \alpha | I_+ I_+ | \alpha \rangle + \langle \beta | I_+ I_+ | \beta \rangle = 0. \end{aligned} \quad (50)$$

We thus obtain

$$\text{Tr}_{(j)} \{ \hat{\rho}_j (\hat{b}_j^{+-}) \} = \frac{1}{2} i B_j P_j \sin \theta_j e^{-i(\omega t_1)}. \quad (51)$$

Similarly

$$\text{Tr}_{(i)} \{ \hat{\rho}_i (\hat{b}_i^{+-})^\dagger \} = \text{Tr}_{(i)} \{ \hat{\rho}_i (B_i \hat{I}_-)_i \} = B_i \text{Tr}_{(i)} \{ \hat{\rho}_i (\hat{I}_-)_i \}$$

giving

$$\text{Tr}_{(i)} \{ \hat{\rho}_i (\hat{b}_i^{+-})^\dagger \} = -\frac{1}{2} i B_i P_i \sin \theta_i e^{+i(\omega t_1)}. \quad (52)$$

Also

$$\begin{aligned} \text{Tr}_{(i)} \{ \hat{\rho}_i (\hat{b}_i^{+-})^\dagger (\hat{b}_i^{+-}) \} &= \text{Tr}_{(i)} \{ \hat{\rho}_i B_i^2 (\hat{I}_-)_i (\hat{I}_+)_i \} \\ &= B_i^2 \text{Tr}_{(i)} \{ \hat{\rho}_i (\hat{I}_-)_i (\hat{I}_+)_i \} \\ &= B_i^2 \text{Tr}_{(i)} \left\{ \frac{1}{2} (\hat{I}_-)_i (\hat{I}_+)_i \right. \\ &\quad \left. + P_i \cos \theta_i (\hat{I}_z)_i (\hat{I}_-)_i (\hat{I}_+)_i \right. \\ &\quad \left. + \frac{1}{2} i P_i \sin \theta_i e^{-i(\omega t_1)} (\hat{I}_-)_i (\hat{I}_-)_i (\hat{I}_+)_i \right. \\ &\quad \left. - \frac{1}{2} i P_i \sin \theta_i e^{+i(\omega t_1)} (\hat{I}_+)_i (\hat{I}_-)_i (\hat{I}_+)_i \right\}. \end{aligned} \quad (53)$$

We now use Eq. (32) again to evaluate the additionally needed traces,

$$\begin{aligned} \text{Tr}_{(i)} \left[(\hat{I}_z)_i (\hat{I}_-)_i (\hat{I}_+)_i \right] &= 0 + \langle \beta | I_z | \beta \rangle = -\frac{1}{2}, \\ \text{Tr}_{(i)} \left[(\hat{I}_-)_i (\hat{I}_-)_i (\hat{I}_+)_i \right] &= 0, \\ \text{Tr}_{(i)} \left[(\hat{I}_+)_i (\hat{I}_-)_i (\hat{I}_+)_i \right] &= 0. \end{aligned} \quad (54)$$

Therefore

$$\text{Tr}_{(i)} \left\{ \hat{\rho}_i (\hat{b}_i^{+-})^\dagger (\hat{b}_i^{+-}) \right\} = \frac{1}{2} B_i^2 (1 - P_i \cos \theta_i). \quad (55)$$

Thus

$$\begin{aligned} (b_{ij}^{+-})_{\text{coh}}^2 &= \text{Tr}_{(i)} \left[\hat{\rho}_i (\hat{b}_i^{+-})^\dagger \right] \text{Tr}_{(j)} \left[\hat{\rho}_j (\hat{b}_j^{+-}) \right] \\ &= \left[-\frac{1}{2} i B_i P_i \sin \theta_i e^{+i(\omega t_1)} \right] \left[\frac{1}{2} i B_j P_j \sin \theta_j e^{-i(\omega t_1)} \right] \\ &= \frac{1}{4} B_i B_j P_i P_j \sin \theta_i \sin \theta_j \end{aligned} \quad (56)$$

and

$$\begin{aligned} (b_i^{+-})_{\text{inc}}^2 &= \text{Tr}_{(i)} \left[\hat{\rho}_i (\hat{b}_i^{+-})^\dagger (\hat{b}_i^{+-}) \right] \\ &\quad - \text{Tr}_{(i)} \left[\hat{\rho}_i (\hat{b}_i^{+-})^\dagger \right] \text{Tr}_{(i)} \left[\hat{\rho}_i (\hat{b}_i^{+-}) \right] \\ &= \frac{1}{2} B_i^2 (1 - P_i \cos \theta_i) - \frac{1}{4} B_i^2 P_i^2 \sin^2 \theta_i \\ &= \frac{1}{2} B_i^2 \left[1 - P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i \right]. \end{aligned} \quad (57)$$

Therefore, the (+−)-type of spin-flip scattering cross section for a collection of nuclei that are well-described by the density operator $\hat{\rho}$ of Eq. (30) is

$$\begin{aligned} \frac{d\sigma^{+-}}{d\Omega} &= \frac{1}{2} \sum_i B_i^2 \left(1 - P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i \right) \\ &\quad + \frac{1}{4} \left\langle \sum_{ij} B_i B_j P_i P_j \sin \theta_i \sin \theta_j e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \end{aligned} \quad (58)$$

The (−+)-case, considered in the same fashion, yields

$$\text{Tr}_{(j)} \left\{ \hat{\rho}_j (\hat{b}_j^{-+}) \right\} = -\frac{1}{2} i B_j P_j \sin \theta_j e^{+i(\omega t_1)} \quad (59)$$

and

$$\text{Tr}_{(i)} \left\{ \hat{\rho}_i (\hat{b}_i^{-+})^\dagger \right\} = \frac{1}{2} i B_i P_i \sin \theta_i e^{-i(\omega t_1)}. \quad (60)$$

Also,

$$\begin{aligned} \text{Tr}_{(i)} \left\{ \hat{\rho}_i (\hat{b}_i^{-+})^\dagger (\hat{b}_i^{-+}) \right\} &= \text{Tr}_{(i)} \left\{ \hat{\rho}_i B_i^2 (\hat{I}_+)_i (\hat{I}_-)_i \right\} \\ &= B_i^2 \text{Tr}_{(i)} \left\{ \hat{\rho}_i (\hat{I}_+)_i (\hat{I}_-)_i \right\} \\ &= B_i^2 \text{Tr}_{(i)} \left\{ \frac{1}{2} (\hat{I}_+)_i (\hat{I}_-)_i \right. \\ &\quad \left. + P_i \cos \theta_i (\hat{I}_z)_i (\hat{I}_+)_i (\hat{I}_-)_i \right. \\ &\quad \left. + \frac{1}{2} i P_i \sin \theta_i e^{-i(\omega t_1)} (\hat{I}_-)_i (\hat{I}_+)_i (\hat{I}_-)_i \right. \\ &\quad \left. - \frac{1}{2} i P_i \sin \theta_i e^{+i(\omega t_1)} (\hat{I}_+)_i (\hat{I}_+)_i (\hat{I}_-)_i \right\} \\ &= \frac{1}{2} B_i^2 (1 - P_i \cos \theta_i). \end{aligned} \quad (61)$$

Thus

$$(b_{ij}^{-+})_{\text{coh}}^2 = \frac{1}{4} B_i B_j P_i P_j \sin \theta_i \sin \theta_j, \quad (62)$$

$$\begin{aligned} (b_i^{-+})_{\text{inc}}^2 &= \frac{1}{2} B_i^2 (1 + P_i \cos \theta_i) - \left\{ \left[\frac{1}{2} i B_i P_i \sin \theta_i e^{-i(\omega t_1)} \right] \right. \\ &\quad \left. \times \left[-\frac{1}{2} i B_i P_i \sin \theta_i e^{+i(\omega t_1)} \right] \right\} \\ &= \frac{1}{2} B_i^2 \left[1 + P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i \right]. \end{aligned} \quad (63)$$

Therefore the (−+)-type of spin-flip scattering cross section is

$$\begin{aligned} \frac{d\sigma^{-+}}{d\Omega} &= \frac{1}{2} \sum_i B_i^2 \left(1 + P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i \right) \\ &\quad + \frac{1}{4} \left\langle \sum_{ij} B_i B_j P_i P_j \sin \theta_i \sin \theta_j e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \end{aligned} \quad (64)$$

We note that for the zero-polarization case, Eqs. (58) and (64) both give the expected result for spin-flip scattering, which is solely incoherent,

$$\frac{d\sigma^{+-}}{d\Omega} = \frac{d\sigma^{-+}}{d\Omega} = \frac{1}{2} \sum_i B_i^2, \quad (65)$$

for a single species the cross section in Eq. (65) becomes $(2/3) N b_{\text{inc}}^2$, where we have used Eq. (48).

It is interesting to note that, unlike the case for zero polarization spin-flip scattering, Eqs. (58) and (64) show that spin-flip scattering from a NMR-prepared, polarized sample can produce $\vec{Q}$ -dependent scattering cross sections, provided that the sample has nonzero polarizations P_i with corresponding values of θ_i that are neither 0 nor π .

V. OBTAINING STRUCTURE FACTORS OF NMR-SELECTED NUCLEI

With use of the cross sections detailed in Eqs. (41), (42), (58), and (64), we now consider possible experiments designed so that sums and differences of their results may give useful information about NMR-selected partial structure factors.

We note first that an experiment that measures the *difference* between the two no-spin-flip cross sections gives no incoherent background and gives structural information that involves the polarization of only one of the nuclei of each pair of nuclei,

$$\left[\left(\frac{d\sigma^{++}}{d\Omega} \right) - \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] = 2 \left\langle \sum_{i \neq j} A_i B_j P_j \cos \theta_j \cos(Q \cdot \vec{r}_{ij}) \right\rangle. \quad (66)$$

Because of the relationship shown in Eq. (43), we note that Eq. (66) is also the cross section that corresponds to the following combination of (++) cross sections, taken at sets of supplementary θ_i values:

$$\begin{aligned} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) - \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] [\text{for } \{\theta_i\}] \\ = \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) [\text{for } \{\theta_i\}] - \left(\frac{d\sigma^{++}}{d\Omega} \right) [\text{for } \{\pi - \theta_i\}] \right]. \end{aligned} \quad (67)$$

Therefore, in the special case in which each $\theta_i = 0$, Eq. (67) gives the polarized neutron scattering contrast that was studied by Buckingham for a square-wave succession of π -pulses in Ref. 1.

A difference experiment that uses the two spin-flip cross sections yields a constant background,

$$\left[\left(\frac{d\sigma^{+-}}{d\Omega} \right) - \left(\frac{d\sigma^{-+}}{d\Omega} \right) \right] = \sum_i B_i^2 P_i \cos \theta_i. \quad (68)$$

For the no-spin-flip cases, if one applies a $\pi/2$ -pulse to all types of nuclei, the scattering cross sections are not sensitive

to the nuclear polarization states, being given by an expression that matches that in Eq. (46),

$$\begin{aligned} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) \right]_{\theta_i=\theta_j=\pi/2} &= \left[\left(\frac{d\sigma^{--}}{d\Omega} \right) \right]_{\theta_i=\theta_j=\pi/2} \\ &= \frac{1}{4} \sum_i B_i^2 + \left\langle \sum_{ij} A_i A_j e^{i\vec{Q} \cdot \vec{r}_{ij}} \right\rangle. \end{aligned} \quad (69)$$

We now consider the *sum* experiment for the no-flip scattering cases,

$$\begin{aligned} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) + \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] &= \frac{1}{2} \sum_i B_i^2 [(1 - P_i^2 \cos^2 \theta_i) + \left\langle \sum_{ij} \left[\left(A_i + \frac{1}{2} B_i P_i \cos \theta_i \right) \left(A_j + \frac{1}{2} B_j P_j \cos \theta_j \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right. \right. \\ &\quad \left. \left. + \left(A_i - \frac{1}{2} B_i P_i \cos \theta_i \right) \left(A_j - \frac{1}{2} B_j P_j \cos \theta_j \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right] \right\rangle] \\ &= \frac{1}{2} \sum_i B_i^2 (1 - P_i^2 \cos^2 \theta_i) + \left\langle \sum_{ij} \left(2A_i A_j + \frac{1}{2} B_i B_j P_i P_j \cos \theta_i \cos \theta_j \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle. \end{aligned} \quad (70)$$

Comparison of Eqs. (70) and (69) suggests that the following combination of the *sum* experiment with the no-spin-flip $\pi/2$ -pulse experiment yields

$$\left(\frac{1}{2} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) + \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] - \left(\frac{d\sigma^{aa}}{d\Omega} \right)_{\theta_i=\theta_j=\pi/2} \right) = \frac{1}{4} \left(\left\langle \sum_{ij} B_i B_j P_i P_j \cos \theta_i \cos \theta_j e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle - \sum_i B_i^2 P_i^2 \cos^2 \theta_i \right), \quad (71)$$

here the superscript “*aa*” indicates the fact that the $\theta = \pi/2$ experiment is a no-spin-flip experiment that could be either (++) or (--), or indeed the average of the two. Provided adequate signal strength, this or closely related experiments could prove very useful indeed, because the structure factor incorporates the polarization of *each* nucleus of a pair, and thus points to the possibility of NMR control of which *pairs* of nuclei contribute to the scattering. By the same token, however, because products of polarizations enter into the cross sections in Eqs. (69) and (71), the corresponding experiments place a more stringent requirement on the needed degree of polarization than would those whose cross sections are represented by Eqs. (66) and (67).

To illustrate the possible use of the experiment described by Eq. (71), we consider the following scenario: suppose one wants to “light up” scattering from a particular spin- $\frac{1}{2}$ nuclear species of just *one* type, call it α , e.g., ^1H , ^{15}N , or ^{13}C . To do so one could apply a sequence of shaped pulses that cause all the *other* types, β , to have $\theta_\beta = \pi/2$, so that $\cos \theta_\beta = 0$ (these “lie down”), while having little effect on the α -type nuclei. When the results of such experiments are combined as in Eq. (71), only terms having $B_i = B_\alpha$ will contribute. For simplicity we also assume that $P_i = P_\alpha$ and $\theta_i = \theta_j = \theta_\alpha$ for all remaining i and j of type α . Under these assumptions, Eq. (71) becomes

$$\begin{aligned} \left(\frac{1}{2} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) + \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] - \left(\frac{d\sigma^{aa}}{d\Omega} \right)_{\theta_i=\theta_j=\pi/2} \right) &= \frac{1}{4} \left(\left\langle \sum_{ij} B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle - \sum_i B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha \right) \\ &= \frac{1}{4} N_\alpha B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha [S_{\alpha\alpha}(\vec{Q}) - 1], \end{aligned} \quad (72)$$

in which

$$S_{\alpha\alpha}(\vec{Q}) = \frac{1}{N_\alpha} \left\langle \sum_{i(\alpha)=1}^{N_\alpha} \sum_{j(\alpha)=1}^{N_\alpha} e^{i\vec{Q} \cdot (\vec{r}_{j(\alpha)} - \vec{r}_{i(\alpha)})} \right\rangle \quad (73)$$

is the structure factor of the α -type nuclei, and N_α is the total number of such nuclei.

If there is a set of nuclear types, say, α , β , and γ , the procedure that results in the cross section shown in Eq. (72) could be applied separately to isolate the structure factors $S_{\alpha\alpha}(\vec{Q})$,

$S_{\beta\beta}(\vec{Q})$, and $S_{\gamma\gamma}(\vec{Q})$. Further, by applying $\pi/2$ -pulses to just the β -nuclei, while leaving the α and γ -type nuclei at suitable rotation angles $\theta_\alpha \neq \pi/2 \neq \theta_\gamma$, one would then be in a

position to determine the cross terms that enter into the partial structure factor $S_{\alpha\gamma}(\vec{Q})$. Specifically, under these conditions Eq. (71) becomes

$$\begin{aligned} \left(\frac{1}{2} \left[\left(\frac{d\sigma^{++}}{d\Omega} \right) + \left(\frac{d\sigma^{--}}{d\Omega} \right) \right] - \left(\frac{d\sigma^{aa}}{d\Omega} \right)_{\theta_i=\theta_j=\pi/2} \right) &= \frac{1}{4} \left(\left\langle \sum_{ij} B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle - \sum_i B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha \right) \\ &+ \frac{1}{4} \left(\left\langle \sum_{ij} B_\gamma^2 P_\gamma^2 \cos^2 \theta_\gamma e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle - \sum_i B_\gamma^2 P_\gamma^2 \cos^2 \theta_\gamma \right) \\ &+ \frac{1}{4} \left\langle \sum_{ij} B_\alpha B_\gamma P_\alpha P_\gamma \cos \theta_\alpha \cos \theta_\gamma e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle \\ &= \frac{1}{4} N_\alpha B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha [S_{\alpha\alpha}(\vec{Q}) - 1] + \frac{1}{4} N_\gamma B_\gamma^2 P_\gamma^2 \cos^2 \theta_\gamma [S_{\gamma\gamma}(\vec{Q}) - 1] \\ &+ \frac{1}{4} \sqrt{N_\alpha N_\gamma} B_\alpha B_\gamma P_\alpha P_\gamma \cos \theta_\alpha \cos \theta_\gamma S_{\alpha\gamma}(\vec{Q}), \end{aligned} \quad (74)$$

in which we have used the definition

$$\sqrt{N_\alpha N_\gamma} S_{\alpha\gamma}(\vec{Q}) = \left\langle \sum_{i(\alpha)=1}^{N_\alpha} \sum_{j(\gamma)=1}^{N_\gamma} \left[e^{i\vec{Q} \cdot (\vec{r}_{j(\gamma)} - \vec{r}_{i(\alpha)})} + e^{-i\vec{Q} \cdot (\vec{r}_{j(\gamma)} - \vec{r}_{i(\alpha)})} \right] \right\rangle, \quad (75)$$

which is similar to the ones found in Refs. 41 and 42; here it is important to note that there are different definitions of partial structure factors $S_{\alpha\gamma}(\vec{Q})$ in use and that the terminology is also used to refer to partial structure factors in which the individual scatterers are taken to be molecules (see, for example, Ref. 4), unlike the usage here.

We anticipate that the pulses needed to prepare experiments to which Eqs. (72) and (74) are applicable can readily be produced because of the widely differing Larmor frequencies of the different nuclei. In principle, one could also imagine such a scheme applied to nuclei that have different chemical shifts, provided that sufficiently selective preparation pulses are practical, given other constraints on the measurement process.

In like fashion to that by which Eqs. (72) and (74) follow from Eq. (71), one can also analyze the difference experiments represented by Eq. (66) or (67) in terms of nuclear types. A possible advantage of such experiments is that only one factor of polarization enters, which may be crucial if the polarization is small. A possible disadvantage is reduced specificity because the polarization of only one of the nuclei of each pair enters. Because of Eq. (67), the elaboration of the difference between the (++) and (--) cross sections in Eq. (66) in terms of different nuclear types would be very much like the analysis of the square-wave pulse scenario previously presented by Buckingham in Ref. 1. Consequently, we do not repeat that analysis here.

We now briefly consider a different type of experimental scenario, but one which we anticipate can still make use of the form of the density operator given by Eq. (30), and hence can be analyzed with use of the cross sections presented above. In this new scenario, instead of removing the sample from the field H_0 at the end of the pulse, one instead leaves the sample in

the static field H_0 and continues to irradiate the sample with the field H_{RF} at the frequency ω , while at the same time measuring the polarized neutron scattering, now *as a function of time*. Such a procedure was mentioned by Buckingham in Ref. 1. For the present we set aside important, relevant considerations of longitudinal and transverse relaxation, as we did for the scenario considered above.

As stated above, in the new, continuous irradiation experiment, we anticipate that a density operator similar to that in Eq. (30) can be used to describe the state of the system at each time t . However, in this new density operator, we substitute the running time of the experiment, t , in place of the pulse length t_p that appears in Eq. (29), which is equivalent to Eq. (30). Because $\omega t_p = (\omega/(\omega_{\text{flip}})_i) \theta_i$, that implies that to study the general nature of the time-dependent cross sections that would result, we can now replace the quantities θ_i by $\gamma_i H_{\text{RF}} (1 - \sigma_i) t$ in the cross sections given above. By doing so, we use a *quasi-static* approximation of time-dependent, but essentially elastic, scattering in introducing this continuous irradiation scenario. We also set aside quantitative treatment of an accompanying inelastic scattering, a possibility that emerges for this experimental scenario in view of the fact that the density operator in the laboratory frame is now a function of time. It is convenient here to note that in elastic scattering, because $k = k'$, the scattering angle θ satisfies $|\vec{Q}| = Q = (4\pi/\lambda) \sin(\theta/2)$.

With use of these approximations for analyzing the continuous irradiation experiment, the (++) cross section given by Eq. (41), as an example, now becomes

$$\begin{aligned} \frac{d\sigma^{++}}{d\Omega}(\vec{Q})[t] &= \frac{1}{4} \sum_i B_i^2 (1 - P_i^2 \cos^2(\omega_i)_{\text{flip}} t) \\ &+ \left\langle \sum_{ij} \left(A_i + \frac{1}{2} B_i P_i \cos(\omega_i)_{\text{flip}} t \right) \right. \\ &\times \left. \left(A_j + \frac{1}{2} B_j P_j \cos(\omega_j)_{\text{flip}} t \right) e^{i\vec{Q} \cdot \vec{r}_{ji}} \right\rangle, \end{aligned} \quad (76)$$

in which $(\omega_i)_{\text{flip}} = \gamma_i H_{\text{RF}} (1 - \sigma_i)$. Thus, the (++) cross section will now exhibit a part that is constant in time that matches the

cross section for unpolarized scattering in Eq. (46), together with superimposed temporal oscillations. Because of the factor $e^{i\vec{Q}\cdot\vec{r}_{ji}}$, some of these oscillations depend on scattering angle θ , while those in the incoherent cross section, combined with the terms $i = j$ in the double sum, will be independent of θ . The frequencies are clearly determined by the factors $\cos[(\omega_i)_{\text{flip}}t]$ and their corresponding products $\cos[(\omega_i)_{\text{flip}}t]\cos[(\omega_j)_{\text{flip}}t]$ and will therefore include all the distinct values of $(\omega_i)_{\text{flip}}$ present in the sample, together with all of their possible sums and differences, $(\omega_i)_{\text{flip}} + (\omega_j)_{\text{flip}}$ and $|(\omega_i)_{\text{flip}} - (\omega_j)_{\text{flip}}|$, respectively.

We note that because the scale of the frequencies $(\omega_i)_{\text{flip}}$ can be controlled experimentally by setting the value of H_{RF} , one has the possibility of adjusting H_{RF} so as to control the frequencies to advantage. This may serve to make measurements practical for a given neutron flux and provide for increasing the validity of the quasi-static approximation.

Thus, in view of the time-dependence of cross sections like that illustrated by Eq. (76), together with possibly useful combinations of such cross sections analogous to those in Eqs. (66)–(75), one can envision a temporal Fourier transform version of NMR spin-modulated, polarized neutron scattering. In this version, the scattering-angle dependences of each component of the Fourier transform of the time-dependent, quasi-static cross sections may in principle be used to measure the structure factors for nuclei with each discernible flip frequency, and for measuring partial structure factors corresponding to each of the *pairs* of nuclear types that have discernible sums or differences of their flip frequencies.

VI. SUMMARY AND CONCLUSIONS

We have developed first-principles expressions for the four types of differential cross sections that would arise in the scattering of polarized neutrons from spin-1/2 nuclei whose spins have been modulated using NMR. In particular, we have considered an NMR pulse that rotates the expectation value of the nuclear spins through a chosen angle, starting from the direction along which both the nuclei and the incident neutrons are initially polarized. For each type of polarized scattering, we have derived generalized structure factors that explicitly show the linear and quadratic dependences of the scattering cross sections on the degree of polarization of each of the sample nuclei. In doing so, we have also identified the incoherent and coherent contributions to the cross sections. While these cross sections agree with the standard ones in the case of an unpolarized sample, more generally they change according to the specific density operator appropriate for the NMR preparation used. We have then considered combinations of the four polarized scattering-experiment types that, in principle, could be used to measure NMR-selected partial structure factors. Finally, we have used our analysis to discuss further¹ the potential for Fourier transform, NMR-modulated polarized neutron scattering.

Further work is needed in order to investigate the feasibility of NMR-modulated neutron scattering. First, it will be useful to calculate the polarized scattering cross sections that would result from use of selective NMR pulse

shaping and sequencing. Second, it is important to find effective ways of optimizing methods of weak-signal detection that take full advantage of (Q, ω) -space, as well as temporal considerations relative to timing of pulses. Third, the formalism needs to be generalized and extended in order to robustly handle target T1/T2 relaxation considerations, as well as alternate experimental scenarios. Fourth, it would be interesting to develop the corresponding scattering cross sections when the spin-decoupling approximations used here are removed. Fifth, analysis of the conditions under which the quasi-static approximation is a good one, and of the possible utility of inelastic scattering, would be of interest in the context of the Fourier transform version. Finally, it would be interesting to extend the present analysis to include nuclei having spin values beyond that of 1/2.

ACKNOWLEDGMENTS

We wish to thank our colleagues George Benedek, Joseph Hornak, and Jeffrey Mills for their suggestions and encouragement. Part of this work was supported by an Eastman Kodak/RIT Chester F. Carlson Center for Imaging Science Innovation Research Grant.

- ¹A. D. Buckingham, *Chem. Phys. Lett.* **371**, 517 (2003).
- ²C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids, Volume 1: Fundamentals*, International Series of Monographs on Chemistry No. 9 (Oxford University Press, Oxford, 1984).
- ³J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Elsevier Academic Press, Amsterdam, 2006).
- ⁴C. G. Gray, K. E. Gubbins, and C. G. Joslin, *Theory of Molecular Fluids, Volume 2: Applications*, International Series of Monographs on Chemistry No. 10 (Oxford University Press, Oxford, 2011).
- ⁵A. Lomakin, N. Asherie, and G. B. Benedek, *Proc. Natl. Acad. Sci. U. S. A.* **96**, 9465 (1999).
- ⁶A. Pande, O. Annunziata, N. Asherie, O. Ogun, G. B. Benedek, and J. Pande, *Biochemistry* **44**, 2491 (2005).
- ⁷J. J. McManus, A. Lomakin, O. Ogun, A. Pande, M. Basan, J. Pande, and G. B. Benedek, *Proc. Natl. Acad. Sci. U. S. A.* **104**, 16856 (2007).
- ⁸P. R. Banerjee, A. Pande, J. Patrosz, G. M. Thurston, and J. Pande, *Proc. Natl. Acad. Sci. U. S. A.* **108**, 574 (2011).
- ⁹J. Cavanagh, W. J. Fairbrother, A. G. Palmer III, M. Rance, and N. J. Skelton, *Protein NMR Spectroscopy: Principles and Practice*, 2nd ed. (Elsevier Academic Press, Amsterdam, 2007).
- ¹⁰C. Shull and R. Ferrier, *Phys. Rev. Lett.* **10**, 295 (1963).
- ¹¹Y. Ito and C. Shull, *Phys. Rev.* **185**, 961 (1969).
- ¹²A. Abragam, G. Bacchella, C. Long, P. Meriel, J. Peisvaux, and M. Pinot, *Phys. Rev. Lett.* **28**, 805 (1972).
- ¹³A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon Press, Oxford, 1982).
- ¹⁴J. Hayter, G. Jenkin, and J. White, *Phys. Rev. Lett.* **33**, 696 (1974).
- ¹⁵O. Halpern and M. Johnson, *Phys. Rev.* **55**, 898 (1939).
- ¹⁶M. Blume, *Phys. Rev.* **130**, 1670 (1963).
- ¹⁷M. Blume, *Phys. Rev.* **133**, A1366 (1964).
- ¹⁸R. Schermer and M. Blume, *Phys. Rev.* **166**, 554 (1968).
- ¹⁹R. Moon, T. Riste, and W. Koehler, *Phys. Rev.* **181**, 920 (1969).
- ²⁰W. Knop, K. Nierhaus, V. Novotny, T. Niinikoski, M. Krumpolc, J. Rieubland, A. Rijllart, O. Schärpf, H. Schink, H. Stuhmann, and R. Wagner, *Helv. Phys. Acta* **59**, 741–746 (1986).
- ²¹M. Van der Grinten, H. Glättli, C. Fermon, M. Eisenkremer, and M. Pinot, *Nucl. Instrum. Methods Phys. Res., Sect. A* **356**, 422 (1995).
- ²²R. Willumeit, N. Burkhardt, G. Diedrich, J. Zhao, K. Nierhaus, and H. Stuhmann, *J. Mol. Struct.* **383**, 201 (1996).
- ²³R. Jünemann, J. Wadzack, N. Burkhardt, M. Schmitt, J. Zhao, H. Stuhmann, and K. Nierhaus, *Phys. B: Condens. Matter* **234**, 193 (1997).
- ²⁴A. Abragam and M. Goldman, *Rep. Prog. Phys.* **41**, 395 (1978).
- ²⁵C. P. Slichter, *Rep. Prog. Phys.* **77**, 072501 (2014).
- ²⁶H. B. Stuhmann, *Physica B: Condens. Matter* **267**, 92 (1999).

- ²⁷H. Glättli, *Nucl. Instrum. Methods Phys. Res., Sect. A* **529**, 194 (2004).
- ²⁸B. Van den Brandt, H. Glättli, I. Grillo, P. Hautle, H. Jouve, J. Kohlbrecher, J. Konter, E. Leymarie, S. Mango, R. May *et al.*, *Eur. Phys. J. B* **49**, 157 (2006).
- ²⁹H. B. Stuhmann, *Appl. Crystallogr.* **40**, s23 (2007).
- ³⁰H. Stuhmann, *J. Phys.: Conf. Ser.* **351**, 012003 (2012).
- ³¹C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer Verlag, Berlin, 1996).
- ³²R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, International Series of Monographs on Chemistry (Oxford University Press, Oxford, 1997), Vol. 14.
- ³³M. Goldman, *Quantum Description of High-Resolution NMR in Liquids* (Oxford University Press, Oxford, 1991).
- ³⁴M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance* (John Wiley & Sons, Chichester, 2006).
- ³⁵M. Tsulaia, *Phys. At. Nucl.* **77**, 1321 (2014).
- ³⁶G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering* (Dover, Mineola, NY, 1996).
- ³⁷S.-H. Chen and M. Kotlarchyk, *Interactions of Photons and Neutrons with Matter*, 2nd ed. (World Scientific, New Jersey, 2007).
- ³⁸G. Navon, Y. Song, T. Room, S. Appelt *et al.*, *Science* **271**, 1848 (1996).
- ³⁹J. H. Lee, Y. Okuno, and S. Cavagnero, *J. Magn. Reson.* **241**, 18 (2014).
- ⁴⁰J.-H. Ardenkjaer-Larsen, G. S. Boebinger, A. Comment, S. Duckett, A. S. Edison, F. Engelke, C. Griesinger, R. G. Griffin, C. Hilty, H. Maeda *et al.*, *Angew. Chem., Int. Ed.* **54**, 9162 (2015).
- ⁴¹J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.* **19**, 774 (1951).
- ⁴²N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **156**, 685 (1967).