A framework for modeling polarized neutron scattering from NMR spin-modulated systems

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Abstract. 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 knowledge of macromolecular or liquid structure.

1. 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. 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. While beautiful theoretical techniques exist to model liquid structure and other properties in terms of intermolecular potentials [2, 3, 4], the uncertainties presently associated with accurately knowing the intermolecular potentials in the first place [5, 6] call for the development of ways to actually measure the intermolecular potentials in undisturbed liquid samples. Another motivating need is that of supplementing current methods of measuring the structure of biological macromolecules.

The basic physical idea behind the present work is to use NMR to take advantage of the nuclear spin-dependent cross sections for neutron scattering. Can one “light up” the nuclei of
one’s choice using NMR to prepare the spin states, then use neutron scattering to see how far apart the selected nuclei are? A key challenge is that very small differences in neutron scattering signals would be associated with the common, very small degrees of nuclear spin polarization. As pointed out in Reference [1], a typical polarization of the sample at room temperature is only on the order of $10^{-5}$. Can small-angle neutron scattering be made sensitive enough to detect these signals?

The present work is intended to lay 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, one can eventually be in a position to quantify the signal-to-noise ratio that would be expected from proposed experimental designs. To start assembling the needed elements we have made a relatively simple choice of NMR modulation, as we describe below.

2. Static scattering cross-section and spin-space decoupling approximation

We begin with a useful form for the ensemble-average elastic cross section for the scattering of polarized neutrons from a spin-polarized target system [7, 8],

$$\frac{d\sigma_{ss'}}{d\Omega} (\vec{Q}) = \left\langle \sum_{i,j} (\hat{b}_{ij}^{s's'})^\dagger (\hat{b}_{ij}^{s's'}) e^{-i\vec{Q} \cdot \vec{r}_j} e^{i\vec{Q} \cdot \vec{r}_j} \right\rangle$$  \hspace{1cm} (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 $\hat{b}_{ij}^{s's'}$ 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 ($<< ... >>$) 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 $I_z$, $I_+$, and $I_-$, respectively, as follows [7]:

$$\hat{b}_j^{++} = (A + B I_z)_j; \quad \hat{b}_j^{--} = (A - B I_z)_j; \quad \hat{b}_j^{+-} = (B I_+)_j; \quad \hat{b}_j^{-+} = (B I_-)_j. \hspace{1cm} (2)$$

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,

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

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 [7, 8].

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, 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.

Consistent with the present decoupling approximation, we rewrite Eq. 1 to distinguish between the spin average, denoted by an overline (⟨...⟩) and the spatial average, denoted by <>. 

\[ \frac{d\sigma^{ss'}}{d\Omega} (\vec{Q}) = \left\langle \sum_{i,j} (\hat{b}_i^{ss'})^\dagger (\hat{b}_j^{ss'}) e^{i\vec{Q}(\vec{r}_j-\vec{r}_i)} \right\rangle \]  

(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 spatial 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 briefly remark on a possibly puzzling fact, namely, that we anticipate that a posteriori knowledge of actual spatial correlations between nuclear positions can in principle be gained from analysis of the dependence of polarized neutron scattering on their joint spin states. It is important to note that these deduced spatial correlations, which result from the interactions of the nuclei with incident neutrons, do not contradict the physical assumption of decoupling of target nuclear spin states from their relative positions.

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, \( \hat{ρ}_{ij,\text{spin}} \):

\[ \langle \hat{b}_i^{ss'} \rangle \langle \hat{b}_j^{ss'} \rangle = T_R \left[ \hat{ρ}_{ij,\text{spin}} (\hat{b}_i^{ss'})^\dagger (\hat{b}_j^{ss'}) \right] \]  

(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: \( \hat{ρ}_{ij,\text{spin}} = \hat{ρ}_{i,\text{spin}} \hat{ρ}_{j,\text{spin}} \), in which \( \hat{ρ}_{i,\text{spin}} \) is the single-nucleus density matrix for nucleus i, and has the property \( T_R \hat{ρ}_{i,\text{spin}} = 1 \). On the other hand, if i = j, we have \( \hat{ρ}_{ij,\text{spin}} = \hat{ρ}_{i,\text{spin}} \). Equivalently, \( \hat{ρ}_{ij,\text{spin}} = (\hat{ρ}_{i,\text{spin}} - \hat{ρ}_{i,\text{spin}} \hat{ρ}_{j,\text{spin}}) \delta_{ij} + \hat{ρ}_{i,\text{spin}} \hat{ρ}_{j,\text{spin}} \). Consequently,

\[ \langle \hat{b}_i^{ss'} \rangle \langle \hat{b}_j^{ss'} \rangle = T_R \left[ \hat{ρ}_i, (\hat{b}_i^{ss'})^\dagger (\hat{b}_j^{ss'}) \right] = T_R(i) \left[ \hat{ρ}_i (\hat{b}_i^{ss'})^\dagger T_R(j) \hat{ρ}_j (\hat{b}_j^{ss'}) \right] \]  

(6)

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

\[
\overline{\langle \hat{b}_i^{ss'} \rangle} \overline{\langle \hat{b}_j^{ss''} \rangle} = \left\{ Tr(i) \left[ \hat{\rho}_i \left( \hat{b}_i^{ss'} \right)^\dagger \left( \hat{b}_j^{ss''} \right) \right] - Tr(i) \left[ \hat{\rho}_j \left( \hat{b}_j^{ss''} \right)^\dagger \left( \hat{b}_i^{ss'} \right) \right] \right\} \delta_{ij} + \\
Tr(i) \left[ \hat{\rho}_i \left( \hat{b}_i^{ss'} \right)^\dagger \right] Tr(j) \left[ \hat{\rho}_j \left( \hat{b}_j^{ss''} \right) \right].
\]

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

\[
\overline{\langle \hat{b}_i^{ss'} \rangle} \overline{\langle \hat{b}_j^{ss''} \rangle} = \left\{ Tr(i) \left[ \hat{\rho}_i \left( \hat{b}_i^{ss'} \right)^\dagger \left( \hat{b}_i^{ss''} \right) \right] - Tr(i) \left[ \hat{\rho}_i \left( \hat{b}_i^{ss''} \right)^\dagger \left( \hat{b}_i^{ss'} \right) \right] \right\} \delta_{ij} + \\
Tr(i) \left[ \hat{\rho}_i \left( \hat{b}_i^{ss'} \right)^\dagger \right] Tr(j) \left[ \hat{\rho}_j \left( \hat{b}_j^{ss''} \right) \right].
\]

We now define coherent and incoherent cross sections as follows:

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

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

in terms of which

\[
\overline{\langle \hat{b}_i^{ss'} \rangle} \overline{\langle \hat{b}_j^{ss''} \rangle} = (b_{ij}^{ss'})^2_{\text{inc}} \delta_{ij} + (b_{ij}^{ss'})^2_{\text{coh}}
\]

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

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

in which \( \mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i \) and \( (b_{ij}^{ss'})^2_{\text{inc}} = \sum_i (b_{ii}^{ss'})^2_{\text{inc}} \). 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.

3. 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. The density operator at time \( t = 0 \) represents the probabilities \( p_+ \) and \( p_- \) that a spin-1/2 nucleus will initially be spin-up and spin-down, respectively, along along the positive z-axis (\( p_+ + p_- = 1 \)). An NMR pulse will subsequently be applied to the sample, and we need to calculate how the density operator changes as a result.

\[
\hat{\rho} (0) = \begin{pmatrix} p_+ & 0 \\ 0 & p_- \end{pmatrix} = \begin{pmatrix} p_+ & 0 \\ 0 & 1-p_+ \end{pmatrix} = \frac{1}{2} \hat{I} + P \left( \frac{1}{2} \right) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2} \hat{I} + P \hat{I}_z
\]

where \( \hat{I} \) 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, and would hold, for example, for a statistical mixture of up and down states in thermal equilibrium.

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. The derivation follows a pattern whose physical basis is given in a number of books, such as [8, 9, 10, 11, 12].

We now briefly describe the nature of the derivation, which will be detailed more completely elsewhere. For nucleus $j$, one first transforms the density operator $\hat{\rho}$ in the laboratory frame to the corresponding density operator $\hat{\rho}_R$ in a frame that is rotating at the RF frequency $\omega$. We assume that the RF frequency is tuned near the relevant Larmor resonant frequency of the nucleus, $\omega_{0i} = \gamma_i H_0 (1 - \sigma_i)$, in which $\gamma_i$ is the gyromagnetic ratio of the $i$th nucleus, $H_0$ is the strength of the static magnetic field applied to the sample, taken to be in the $z$-direction, and $\sigma_i$ is the chemical shift of nucleus $i$. This transformation to the rotating frame takes the form 

$$\hat{\rho}_R = \hat{R}^{-1} \hat{\rho} \hat{R},$$

in which $\hat{R} = \exp(i\omega t \hat{I}_z)$. In the rotating frame, the effective Hamiltonian is time-independent, allowing for the treatment below.

At time $t = 0$, clearly $\hat{\rho}_R(0) = \hat{\rho}(0)$. At the end of the pulse, which we take to have duration $t_p$, $\hat{\rho}_R(t_p) = \hat{T}^{-1} \hat{\rho}_R(0) \hat{T}$, in which $\hat{T} = \exp(i \hat{H}_{\text{eff}} t_p / \hbar)$ and in turn, $\hat{H}_{\text{eff}} \approx -\gamma_j \hbar H_{\text{RF}}(1 - \sigma_j) \hat{I}_z$, in which $H_{\text{RF}}$ is the strength of the radio-frequency magnetic field and $\hat{I}_z$ is the $x$-component angular momentum operator for nucleus $j$; this form of $\hat{H}_{\text{eff}}$ assumes that the pulse is in the negative $x$-direction in the rotating frame. The effect of the pulse can be summarized by the so-called “spin-flip” frequency, $\omega_{\text{flip}} = \gamma_i H_{\text{RF}}(1 - \sigma_j)$; in particular, as a result of the pulse, the direction of the expected nuclear spin polarization rotates by an angle $\theta_i = (\omega_{\text{flip}}) t_p$ from the $z$-axis. Finally, one transforms the density operator back to the laboratory frame, that is, the frame in which we are calculating neutron scattering cross sections, with use of $\hat{\rho}(t_p) = \hat{R} \hat{\rho}_R(t_p) \hat{R}^{-1}$.

Immediately following the pulse, the density operator in the laboratory frame can be shown by the full derivation to become

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

(14)
or, in terms of the raising and lowering operators for nucleus $i$, and using $\omega t_p = \omega/(\omega_{\text{flip}})_i \theta_i$,

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

(15)

Use of the raising and lowering operators, as in Eq. 15, greatly simplifies the evaluation of the traces over spin states needed to evaluate the scattering cross-sections in Eqs. 9 and 10.

4. Polarized 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. 15. 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. 15 is a good model.

We now use Eq. 15 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 the initial rotation angle $\theta_i$, 

$$
$$
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

$$T r(j)[\hat{\rho}_j(\hat{b}_j^{++})] = T r(j)[\hat{\rho}_j(A_j + B_j(\hat{I}_z)_j)]$$

(16)

and

$$T r(j)[\hat{\rho}_i(\hat{b}_i^{++})] = T r(j)[\hat{\rho}_i(A_i + B_i(\hat{I}_z)_i)(A_i + B_i(\hat{I}_z)_i)]$$

(17)

Upon evaluating the result of substituting the expression for $\hat{\rho}_j$ from Eq. 15 into Eq. 16,
evaluating the trace, then using Eq. 9, one obtains

$$(b_{ij}^{++})^2_{coh} = (A_i + \frac{1}{2}B_i P_i \cos \theta_i)(A_j + \frac{1}{2}B_j P_j \cos \theta_j).$$

(18)

By similarly evaluating the trace in Eq. 17 and using that result together with the one from
Eq. 16 in Eq. 9, one obtains

$$(b_{i}^{++})^2_{inc} = \frac{1}{4}B_i^2(1 - P_i^2 \cos^2 \theta_i)$$

(19)

The details of this derivation will be published elsewhere. Upon inserting Eqs. 18 and 19 into
Eq. 12, the (++) cross section takes the form

$$\frac{d\sigma^{++}}{d\Omega}(\hat{Q}) = \frac{1}{4} \sum_i B_i^2(1 - P_i^2 \cos^2 \theta_i) + \langle \sum_{ij}(A_i + \frac{1}{2}B_i P_i \cos \theta_i)(A_j + \frac{1}{2}B_j P_j \cos \theta_j)e^{i\hat{Q}\cdot\hat{r}_{ij}} \rangle$$

(20)
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. 20 with \(-B_i\), giving

\[
\frac{d\sigma^{--}}{d\Omega}(\vec{Q}) = \frac{1}{4} \sum_i B_i^2 (1 - P_i^2 \cos^2 \theta_i) + \left( \sum_{ij} (A_i - \frac{1}{2} B_i P_i \cos \theta_i)(A_j - \frac{1}{2} B_j P_j \cos \theta_j) e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

(21)

We find that the second terms on the right-hand sides of Eqs. 20 and 21, when specialized to \(\theta_i = \theta_j = 0 \) or \(\pi\), are consistent with the result obtained by Buckingham, as specified in the second term on the right-hand side of Eq. 4 of reference [1], with use of Eq. 2 of that paper; we note that reference 1 considered only the effect of \(\pi\)-pulses. However, we also find that the first, or incoherent terms in Eqs. 20 and 21 differ from the corresponding term in Eq. 4 of [1]. Details will be given in another publication.

Eqs. 20 and 21 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

\[
(b_{ij}^{++})^2_{coh} = (b_{ij}^{--})^2_{coh} = A_i A_j \quad \text{and} \quad (b_{ij}^{++})^2_{inc} = (b_{ij}^{--})^2_{inc} = \frac{1}{4} B_i^2 \quad \text{(for } P_i = P_j = 0\text{)}
\]

(22)

giving

\[
\frac{d\sigma^{++}}{d\Omega}(\vec{Q}) = \frac{d\sigma^{--}}{d\Omega}(\vec{Q}) = \frac{1}{4} \sum_i B_i^2 + \left( \sum_{ij} A_i A_j e^{i\vec{Q} \cdot \vec{r}_{ij}} \right) \quad \text{(for } P_i = P_j = 0\text{)}.
\]

(23)

For \(N\) unpolarized target nuclei of a single spin \(\frac{1}{2}\) species, Eq. 23 reduces further to the expected result for the no spin-flip case for scattering from an unpolarized target [7, 8, 2]

\[
\frac{d\sigma^{++}}{d\Omega}(\vec{Q}) = \frac{d\sigma^{--}}{d\Omega}(\vec{Q}) = \frac{1}{3} N b_{inc}^2 + \left( \sum_{ij} A_i^2 e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

\[
= \frac{1}{3} N b_{inc}^2 + N A^2 \left( \frac{1}{N} \sum_{ij} e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

\[
= \frac{1}{3} N b_{inc}^2 + N A^2 S(\vec{Q})
\]

(24)

in which \(S(\vec{Q})\) is the static structure factor, and in which we have used the definition [8]

\[
b_{inc}^2 = I(I + 1)B^2 = \frac{3}{4} B^2.
\]

(25)

For the \((+-\)\) case, i.e. neutron spin-flip scattering, evaluation of the needed traces gives

\[
(b_{ij}^{+-})^2_{coh} = \frac{1}{4} B_i B_j P_i P_j \sin \theta_i \sin \theta_j
\]

(26)

and

\[
(b_{ij}^{+-})^2_{inc} = \frac{1}{2} B_i^2 [1 - P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i].
\]

(27)

Again, details of this derivation will be published elsewhere. Using Eqs. 26 and 27 in Eq. 12 gives the scattering cross section

\[
\frac{d\sigma^{+-}}{d\Omega} = \frac{1}{2} \sum_i B_i^2 (1 - P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i) + \frac{1}{4} \left( \sum_{i,j} B_i B_j P_i P_j \sin \theta_i \sin \theta_j e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

(28)
For \((\pm)\) neutron spin-flip scattering, one has
\[
(b_{i,j}^{\pm})^2_{\text{coh}} = \frac{1}{4} B_i B_j P_i P_j \sin \theta_i \sin \theta_j
\]  
(29)

and
\[
(b_{i}^{\pm})^2_{\text{inc}} = \frac{1}{2} B_i^2 [1 + P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i].
\]  
(30)

giving
\[
\frac{d\sigma^\pm}{d\Omega} = \frac{1}{2} \sum_i B_i^2 \left(1 + P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i\right) + \frac{1}{4} \left< \sum_{i,j} B_i B_j P_i P_j \sin \theta_i \sin \theta_j e^{i \mathbf{Q} \cdot \mathbf{r}_{ij}} \right>
\]  
(31)

For the zero-polarization case, Eqs. 28 and 31 both give the expected result for spin-flip scattering, which is solely incoherent:
\[
\frac{d\sigma^+}{d\Omega} = \frac{d\sigma^-}{d\Omega} = \frac{1}{2} \sum_i B_i^2;
\]  
(32)

for a single species the cross-sections in Eq. 32 become \((2/3) N b_{\text{inc}}^2\), where we have used Eq. 25.

5. Obtaining structure factors of NMR-selected nuclei

With use of the cross sections detailed in Eqs. 20, 21, 28, and 31, 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 structural information for which the polarization of only one of the nuclei in each pair of nuclei enters:
\[
\left[\left(\frac{d\sigma^+}{d\Omega}\right) - \left(\frac{d\sigma^-}{d\Omega}\right)\right]_{\theta_i = \theta_j = \pi/2} = \frac{1}{2} \left< \sum_{i \neq j} A_i B_i P_i \cos \theta_i \cos (Q \cdot \mathbf{r}_{ij}) \right>
\]  
(33)

A difference experiment that uses the two spin-flip cross sections yields a constant background:
\[
\left[\left(\frac{d\sigma^+}{d\Omega}\right) - \left(\frac{d\sigma^-}{d\Omega}\right)\right] = \frac{1}{2} \left< \sum_i B_i^2 \left[1 + P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i\right] - \left[1 - P_i \cos \theta_i - \frac{1}{2} P_i^2 \sin^2 \theta_i\right] \right>
\]  
(34)

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. 23:
\[
\left[\left(\frac{d\sigma^+}{d\Omega}\right)\right]_{\theta_i = \theta_j = \pi/2} = \left[\left(\frac{d\sigma^-}{d\Omega}\right)\right]_{\theta_i = \theta_j = \pi/2} = \frac{1}{4} \sum_i B_i^2 + \left< \sum_{i,j} A_i A_j e^{i \mathbf{Q} \cdot \mathbf{r}_{ij}} \right>
\]  
(35)
We now consider the *sum* experiment for the no spin-flip scattering cases:

\[
\left[ \left( \frac{d\sigma^{++}}{d\Omega} \right) + \left( \frac{d\sigma^{--}}{d\Omega} \right) \right] = \frac{1}{2} \sum_i B_i^2 \left[ (1 - P_i^2 \cos^2 \theta_i) + \sum_{ij} \left[ (A_i + \frac{1}{2} B_i P_i \cos \theta_i)(A_j + \frac{1}{2} B_j P_j \cos \theta_j) e^{i\vec{Q} \cdot \vec{r}_{ij}} \right] \\
+ (A_i - \frac{1}{2} B_i P_i \cos \theta_i)(A_j - \frac{1}{2} B_j P_j \cos \theta_j) e^{i\vec{Q} \cdot \vec{r}_{ij}} \right] \right)
\]

\[
= \frac{1}{2} \sum_i B_i^2 (1 - P_i^2 \cos^2 \theta_i) + \sum_{ij} \left( 2A_i A_j + \frac{1}{2} B_i B_j P_i P_j \cos \theta_i \cos \theta_j e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

(36)

Comparison of Eqs. 36 and 35 suggests that the following combination of the *sum* experiment with the no spin-flip $\pi/2$-pulse experiment yields

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

(37)

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.

Finally, we consider another possible scenario: suppose one wants to “light up” scattering from a particular spin-$\frac{1}{2}$ nuclear species of just one type, call it $\alpha$, e.g. $^1$H, $^{15}$N, or $^{13}$C. To do so one could apply a sequence of shaped pulses that cause all the other types, $\beta$, to have $\theta_\beta = \pi/2$, so that $\cos \theta_\beta = 0$ (these “lie down”), while having little effect on the $\alpha$-type nuclei. When the results of such experiments are combined as in Eq. 37, 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 $\alpha$. Under these assumptions, Eq. 37 becomes

\[
\left\{ \frac{1}{2} \left[ \left( \frac{d\sigma^{++}}{d\Omega} \right) + \left( \frac{d\sigma^{--}}{d\Omega} \right) \right] - \left( \frac{d\sigma^{aa}}{d\Omega} \right)_{\theta_i=\theta_j=\pi/2} \right\} = \frac{1}{4} \left[ \sum_{ij} B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha e^{i\vec{Q} \cdot \vec{r}_{ij}} \right] - \sum_i B_\alpha^2 P_\alpha^2 \cos^2 \theta_\alpha)
\]

(38)

in which

\[
S_{aa}(\vec{Q}) = \frac{1}{N_\alpha} \left( \sum_{ij} e^{i\vec{Q} \cdot \vec{r}_{ij}} \right)
\]

(39)

is the structure factor of the $\alpha$-type nuclei, and $N_\alpha$ is the total number of such nuclei. We anticipate that the pulses needed to prepare experiments to which Eq. 38 is 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.
6. Summary and Conclusions

In summary, we have developed first-principles expressions for the four types of polarized differential cross-sections that would arise in the scattering of polarized neutrons from 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, which agree with the standard ones in the case of an unpolarized sample. Finally, we have considered potentially useful combinations of the four polarized scattering-experiment types that, in principle, could be used to measure NMR-selected partial structure factors.

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 $(Q, \omega)$-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, such as performing neutron scattering while the target remains in the NMR fields. Fourth, it would be interesting to develop scattering cross-sections when the spin-decoupling approximations used here are removed.

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