

Magn. Reson. Discuss., author comment AC3
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Reply on RC2

Günter Hempel et al.

Author comment on "Efficient polynomial analysis of magic-angle spinning sidebands and application to order parameter determination in anisotropic samples" by Günter Hempel et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2021-39-AC3>, 2021

We thank Anonymous Referee #2 for comments and questions which helped to improve the way of explaining our results, add some necessary details and remove some errors.

Comment: This paper introduces an exact polynomial representation of SSB intensities to overcome the "far too complicated to be applied", in the words of the authors, Herzfeld-Berger relation.

Response: Here we refer to the powder average over a threefold sum from $-\infty$ to $+\infty$ over products of Bessel functions as analytical expression (equation (25) of this paper) which is of course an important result, but a polynomial seems to have a simpler structure. Furthermore, if χ^2 has to be calculated in dependence on two, three, ..., parameters where the multiply repeated calculation of SSB is required, the polynomial should be clearly advantageous.

However, we will weaken this phrase to "rather complicated equation (25)".

Comment: The first question that comes up is the justification that the polynomial evaluation will be appreciably faster than a numerical powder average of the expression that is routinely used.

Response:

- Calculation of powder average in a numerical simulation requires one or two loops around the calculation of SSB (for example using a REPULSION dataset with say 1000 points, or a independent variation of polar and azimuthal angle with a sufficient number of steps). In the *polynomial* formulae introduced here, the *powder average is already included!*
- Multidimensional χ^2 calculation for a multitude of n -tuples {par1, par2, ...} is expected to be simpler and faster if a polynomial is used instead a program or a subroutine; furthermore
- a simple polynomial can be better included into a fitting routine than a program. For example Newton procedure or Levenberg-Marquardt procedure demand calculation of first derivatives.

This comment was helpful in the sense that we will add to the paper a rough back-of-the-envelope estimation of the improvement in calculation efficiency.

Comment: Secondly, it is not clear how the polynomial expression that is obtained is exact, as is claimed; it is an approximation to some order.

Response: The polynomials for the SSB of the isotropic case are exact if they would be summed up to infinity. This becomes clear from the derivation of the formula: All included series (binomial) and expressions are used without any approximation. Of course, practically one has to restrict to a maximum power. However this can be chosen to get arbitrary accuracy.

Comment: That said, there are some interesting aspects to the paper. Taking sum and difference of positive and negative sidebands of a particular order is one such. Is this only true for polynomial expansion or is it general? So also is the use of symbolic manipulation programs for evaluating the coefficients.

Response: The qualitative issue does not depend on using polynomial description or another. But it seems that it can be expressed advantageously in a mathematical fashion if the polynomial representation is used. Especially the fact that the odd powers change the sign between positive and negative sidebands, the even powers not, imply an easy possibility for the representation of sum and difference. We will add an explanation of this issue.

Question: It is understandable that in successive rotations the last rotation of the previous rotation and the first rotation of the present can be combined because they are about the same axis. However, wouldn't the first rotation of the first and the last rotation of the last remain?

Response: Of course, the last rotation remain. Yet this is a rotation around \mathbf{B}_0 (after the magic-angle flip) which has no meaning here and is never performed. The first rotation is member of the first $\mathbf{R}_z - \mathbf{R}_y$ doubly rotation.

Comment: Because of performing rotations in the vector space spanned by the tensors, rotations are treated as a left multiplication with a 5 x 5 matrix. The advantage that this affords over bilinear matrix operations would depend on the number of multiplication and addition operations involved, and not on the size (storage is a minor factor).

Response: Yes, we agree concerning the importance of number of operations and will clarify the statement. (This is related probably to lines 95 ... 106. But concerning the last part of this comment, it was not clear to which position of the manuscript the referee refers to.)

Question: In equation 25 (and may be a few others), the coefficients vary over orders of magnitude with some of the coefficients being extremely small. Are these small coefficients really significant?

Response: Whether or not they are significant, depends on the variable w . For example the realistic case of parameters $\eta = 1$ and $(\omega_0\delta / \omega_r) = 3$ gives $w = 6$; and $6^{12} > 2 \times 10^9$ leads to significance also of coefficients in the order 10^{-10} .

Comment: In Figure 2, one find that the I_+ intensity for the 12th order polynomial lies between 6 and 12. Increase the order would make it go further towards 2? That looks counterintuitive.

Response: This might appear if you observe the position $w = 6$ only. However if we

consider the whole curve: the second-order polynomial is simply a parabola which will never be fitted by the 12-order polynomial. Moreover, there MUST be a crossing at some point because the parabola grows unlimited but not I_+ . For an example, please imagine the Taylor series of sin or cos functions: Because of alternating signs within the series we get an up and down of the function during enhancing the order.

Question: In Figure 4, what are the triangles and what is the red curve?

Response: Thank you - it must be added for the revised version that the triangles are experimental data and the red curve is the fit on the polynomial formula.

Comment: Something is missing from the sentence starting at the end of line 321.

Response: This sentence will be corrected in the revised version.

Question: Why is the δ of C1 and C2 in Table 2 different from that on line 374?

Response: Did I misunderstand your question? For my opinion, the δ values in line 374 are EQUAL to that in table 2.

Comment: Equation 38 assumes that C2 and C5 are polarized identically despite the protons around them being two bonds apart in one case and three bonds apart in the other.

Response: For both carbons, the nearest protons are those two which are bound to the neighbouring aromatic carbons (C3 and C4, resp.), i.e. two bonds apart. This is equal distance, and therefore we assumed that the polarization of both C2 and C5 are very similar.

Question: What is the origin of equation 39?

Response: A note on the origin of this equation is missing and will be added in the revised version. For obtaining this equation, we have played with the coefficients of I_{-2} , I_{-1} , I_1 and I_2 until the oscillation along t_1 vanishes. The aim was as explained in the text a check if the CP efficiency was stable over the long-lasting experiment.