Reply on CC3
Malcolm H. Levitt and Christian Bengs

Author comment on "Hyperpolarization and the Physical Boundary of Liouville Space" by Malcolm H. Levitt and Christian Bengs, Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-26-AC4, 2021

Thanks to Geoffrey for the typically insightful commentary, although I have some points of difference (falling well short, however, of a "furious argument").

Geoffrey draws an analogy between the straight edges of the physical bounds with the straight path traced by the tip of a recovering magnetization vector for spins-1/2 in the case T1=T2. However I think the resemblance is deceptive and largely accidental. The tip of a recovering magnetization vector does not trace a straight path if T1 ≠ T2 and in the extreme limit T1=T2/2 (rarely encountered, but possible), the tip of the vector clings to the surface of the Bloch sphere. So I don't think this analogy is anything other than accidental.

Geoffrey follows with a speculation that including series expansion terms beyond the double commutator might lead to convergence to the Lindblad expressions. I do not think so, although I hope that my co-author Christian can comment. The breakdown of the semiclassical double-commutator form of the relaxation superoperator, in the case of a finite environmental temperature, is independent of the quantity | omega_fluc tau_c |, where omega_fluc is some measure of the size of the fluctuating terms, and tau_c is their correlation time. The Redfield regime is valid when this quantity is small, but the double-commutator expressions lack strict validity whatever the size of this quantity. That would not be expected if additional perturbation terms were relevant.

The next comment concerns the handling of coherences in our paper. It is true that consideration of coherences is largely excluded, which is a defect. We expect to address some of these issues at a later date, and some comments to that effect will be added at the end of the paper. The lack of distinction between populations and zero-quantum coherences is, on the other hand, deliberate, since this distinction is not relevant. The treatment and the bounds we sketch are independent of the chosen basis (except for a uniform rotation of the bounding shape). Populations in one basis may be zero-quantum coherences in a different basis. Nevertheless we will try to clarify that.

It is true that the "bare triangle" could indeed be fleshed out in additional dimensions. Some representations of the resulting shapes may be found in some of the cited mathematical physics literature, for example Figs 2 to 8 in https://doi.org/10.1088/1751-8113/49/16/165203.
Geoffrey raises the issue of long-lived coherences, for example between the singlet and triplet states in spin-1/2 pairs. Just as a point of accuracy, our paper doi.org/10.1103/PhysRevLett.103.083002 introduced this concept before the Karthik paper. As far as the current paper is concerned, it is true that we do not consider the physical bounds on these coherences, and indeed on any operators for spin-1/2 pairs that are not symmetric with respect to spin exchange (this is stated explicitly). Again, this topic has to be deferred for further study. It would be gratifying if some other research groups became interested in this rather arcane topic.

I have stated my views elsewhere in the discussion on the semantic merits of using "polarization" to imply more general states than those which have a net orientation of magnetic moments with an external direction. Although I see the objection I also worry that introducing a neologism such as "hyperorder" to represent a more general state than "hyperpolarization" is impractical and will not catch on. I propose simply accepting that the meaning of "polarization" might be extended beyond its linguistic roots, as happens all the time for other words. But obviously this is a matter of opinion and the issue can probably only be settled by eventual adoption and usage by the community.

Geoffrey likes the term "population imbalance" and dislikes "singlet polarization". I agree that "singlet order" is better (although see above). However my interpretation is that a system in a state of singlet order displays a population imbalance between the singlet and triplet states. In other words, these terms are not synonymous. A "singlet-triplet population imbalance" is an attribute of the presence of "singlet order".

Geoffrey proposes the use of symbol $T_{\lambda\mu}$ which "says it all". Unfortunately this symbol does not "say it all". The spherical tensor operator components $T_{\lambda\mu}$ used by the NMR community are not normalized, while the NISTOs are. That is why a different font face was introduced for these operators. I see this is clumsy but I could see no better alternative.

I do not agree with the suggestion that the term "coefficients" could somehow be used instead of "polarization moments". The term "coefficients" is an abstract mathematical term, simply meaning the multiplying factors or certain expressions, and does not imply anything about the physics of the system. The term "polarization moments" is used for the coefficients of spherical tensor operators in a multipole expansion of the density operator. I think the connection with atomic physics usage is healthy and that the magnetic resonance community has much to gain by better contact with such fields.

The term "exceedingly" should indeed be made more precise.

I do not understand the problem with the scales of Fig.2. All terms are defined in the paper. I do not see what more we can do.

It is not true that the discussion of spin-1/2 pairs is only valid for magnetically equivalent pairs. The properties of these operators is independent of the basis, and in particular, independent of the spin Hamiltonian and its eigenbasis.

The illuminating intention of Geoffrey's arguments are fully recognized, and appreciated. However, if he wants another furious argument, I stand ready!

I agree that this sort of discussion on a paper prior to publication is refreshing and valuable. Thanks to the founders of Magnetic Resonance for enabling it!