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Comment on mr-2021-6

Anonymous Referee #2

Referee comment on "Simple rules for resolved level-crossing spectra in magnetic field effects on reaction yields" by Dmitri V. Stass et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-6-RC2, 2021

The simplest model for analysing the spin dynamics of radical pairs is the so-called 'exponential model' and the simplest description of radical pair spin-state evolution is under the action of a spin Hamiltonian that contains only electron Zeeman and hyperfine coupling terms for each of the individual radical pair partners. This description of radical pairs has long been used to provide useful insights into the behaviours of radical pairs and in particular is often the starting point for simulation of dependence of magnetic field effects on applied magnetic field strength - the so-called MARY curve. In this work the authors take a new analytical approach to deconstructing the predictions of this model. This results in a set of rules that provide very useful insights into both the key features of MARY curves, but that also predict the ability to use MARY as a spectroscopic method yielding spectra effectively equivalent to conventional ESR spectra under particular constraints of the relative hyperfine structure of the pair partners.

I believe that the analytical approach is an extremely useful one, with important predictive power. In particular, I found that the insight it provides over the essential 'canceling' of crossings and anti-crossings and the resulting impact on, for example, the so-called 'low-field effect (LFE)' highly enlightening. In this particular case (and indeed perhaps more so in the other cases discussed) the rules and analytical framework might lead to important new usage cases for 'MARY spectroscopy.' The authors do a good job of relating this approach back to existing ones and highlighting the new insights as well as confirming that it leads to the same existing predictions and understanding.

Therefore, I have no hesitation in recommending that this paper be published as is. However, I do have some observations that the authors may wish to consider (i.e. these are fully optional but may be worth giving some thought to).

1) Accessibility

The paper is clearly written and while it contains a large number of equations, it is quite straightforward and logical to follow. However, I think the lack of any visual representation of the findings is to some extent a missed opportunity. I feel that in the key example domains the authors consider, it might be useful to provide example spectra and highlight the features that the interpretation is pointing at. Personally I find some problems easier to think about mathematically and others visually. By providing an additional visual representation, it may increase the accessibility of the findings to a broader audience.

2) Extensions

As I indicated at the beginning of this comment, the rules are based on a very simple model of RP reactions which does not account for electron exchange or dipolar interactions, incoherent spin relaxation or spin-selective reaction (to name a few). Given the importance of some of these factors, particularly in relation to some of the realistic example systems provided, I wonder if the authors could say even a little about how some of these factors might influence the simple predictions? This may also be useful to experimentalists in thinking about real systems that can exploit some of the predictions provided.

3) Small errors.

I provide no adjustment to grammatical errors in the manuscript, but I did notice a small number of typographical errors that either directly impact the scientific meaning, affect technical terms or may confuse. I list these below:

- Line 195 ‘produce crossings Of Eq. (7)’ —> ‘produce crossings of Eq. (7)’
- Line 343 ‘in addition to for equivalent fluorines’ —> ‘in addition to four equivalent fluorines’
- Line 354 ‘donor-acceptor diads’ —> ‘donor-acceptor dyads’