This paper describes dissolution DNP-NMR experiments for a variety of reaction schemes using the Bloch-McConnell equations. The topic of the paper is very timely, given the current intense interest in DNP approaches; however, in present form, the main contributions of the paper are difficult to discern.

1. A great deal of the paper recapitulates the work published as:

Kuchel, P. W., and Shishmarev, D.: Dissolution dynamic nuclear polarization NMR studies of enzyme kinetics: Setting up differential equations for fitting to spectral time courses, J. Magn. Reson. Open, 1, 100001, doi.org/10.1016/j.jmro.2020.100001, 2020.

and at least to this reviewer, the novel aspects of the present paper are not clearly distinguished from the earlier work. This could be addressed by an appropriate summary in the conclusion.

I do not understand the statements at line 260-265:

> The equilibrium constant was fixed so that $K = k_1/k_{-1} = 2$; hence the system was not at chemicalcequilibrium at t = 0 s. The simulations highlight an important point: In the absence of exchange the Bloch-McConnell equations predict the recovery of the z magnetizations back to their equilibrium values $M_{z,eq}^{A}$ and $M_{z,eq}^{B}$ while under conditions of fast exchange this no longer holds, and a non-equilibrium system will rapidly return to its chemical equilibrium, not to its thermal equilibrium, within the timescale of the NMR experiment; specifically within five T_1 values.

If the system is not at chemical equilibrium, $M_{z,eq}^{A}$ and $M_{z,eq}^{B}$ are not constants as represented in Eq. 19. Rather, these quantities become time-dependent, for example:

$$M_{z,eq}^{A}(t) = M_0 \frac{[A(t)]}{[A(t)]+[B(t)]}$$

$$M_{z,eq}^{B}(t) = M_0 \frac{[B(t)]}{[A(t)]+[B(t)]}$$

as shown in Eq. 2.4.18 of Ernst et al. (Ernst, R. R., Bodenhausen, G., and Wokaun, A.: Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987). Thus, it is unclear what is shown in Fig. 1 (which the text indicates is based on Eq. 19) and hence what is meant by the above statement.

Section 4 of the paper expands the dimensionality of the Bloch-McConnell equations to include the molecules that are not hyperpolarized by the DNP. Thus A*(t) represents hyperpolarized species and A(t) represents the unpolarized species, with A*(t) + A(t) = [A(t)] is the total concentration of A at time t (and similarly for B). The authors then numerically solve the four coupled differential equations. This is somewhat misleading in my view. Applying a similarity transformation to Eq. 39 with the matrix:

$$S = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$$

separates the four equations to two independent sets of equations. One set is a pair of coupled differential equations for A*(t) (Eq. 37) and B*(t) (Eq. 38), describing the evolution of the hyperpolarized magnetization and another set (Eq. 40) describing the evolution of [A(t)] and [B(t)]. That is, the hyperpolarized magnetization just evolves according to the normal Bloch-McConnell equations and the chemical system evolves to chemical equilibrium, as expected (note that this situation would be more complicated if time-dependent steady state magnetizations were included as above, but these terms are small and neglected in this section of the paper, given the large DNP enhancements). A four-dimensional set of equations do not need to be solved. I have not checked whether any of the other more complicated schemes presented in the rest of the paper can be similarly decomposed, but it is essential that the authors clarify this issue.

Minor:

Eqs. 19 and 20 seem to be missing a leading minus sign on rhs.