Magn. Reson. Discuss.,
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Interactive comment on "Revisiting paramagnetic relaxation enhancements in slowly rotating systems: how long is the long range?" *by* Giovanni Bellomo et al.

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We are grateful to Gottfried Otting for his constructive comments, which helped us to make the message clearer and more complete. Here below please find our answers. The manuscript will be modified accordingly.

Comment 1. Interestingly, at intermediate distances the opposite effect can occur too, i.e. the total PRE can become slower than expected based on the simple Solomon equation. Is this due to NOE contacts with protons located at greater distance from the paramagnetic centre?

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Answer: As noticed, at intermediate distances the total PRE can actually become slightly slower than expected from the Solomon equation. This is indeed caused by the dipole-dipole interactions with protons at larger distances from the paramagnetic metal, which cause “magnetization losses” from the closer to the farther protons. This is clarified by an additional simple simulation where 6 protons are placed along a straight line at 10, 12, 14, 16, 18 and 20 Å from a gadolinium ion. The results of the simulation are shown in the figure S6 below. The magnetization of the proton at 10 Å recovers its equilibrium value slower than predicted from an exponential behavior, so that the monoexponential fit provides a longer relaxation time. The figure also shows (black dotted lines) the magnetization curves expected from the Solomon equation for the two protons at 10 and 20 Å. Clearly the first points of the magnetization recovery for the proton at 10 Å agree with the relaxation rate predicted by the Solomon equation. This comment will be introduced in the revised version, and the figure S6 will be added in the Supplement.

Comment 2. Can the authors predict what the situation would be like for backbone amide protons in a perdeuterated protein in H2O, where the only protons are the amide protons from the backbone and side chains (also allowing the presence of hydroxyl protons)? What would the situation be like if the methyls of isoleucine, valine and leucine are protonated whereas the rest of the protein is perdeuterated?

Answer: We have performed the suggested calculations. As shown in Fig. S7A, amide and hydroxyl protons in perdeuterated conditions almost recover the rates predicted by the Solomon equation, although a slight smaller distance can anyway be calculated for protons at more than 20 Å from the paramagnetic metal. Methyl protons fully recover the Solomon behavior if the rest of the protein is perdeuterated (Fig. S7C). These plots will be added to the Supplement of the revised version.

Comment 3. Line 136: exchange rates usually are expressed in s-1, not seconds. Answer: In the revised version we will write “with an exchange rate of 10ˆ4 sˆ-1”. Thank you for having pointed this out.

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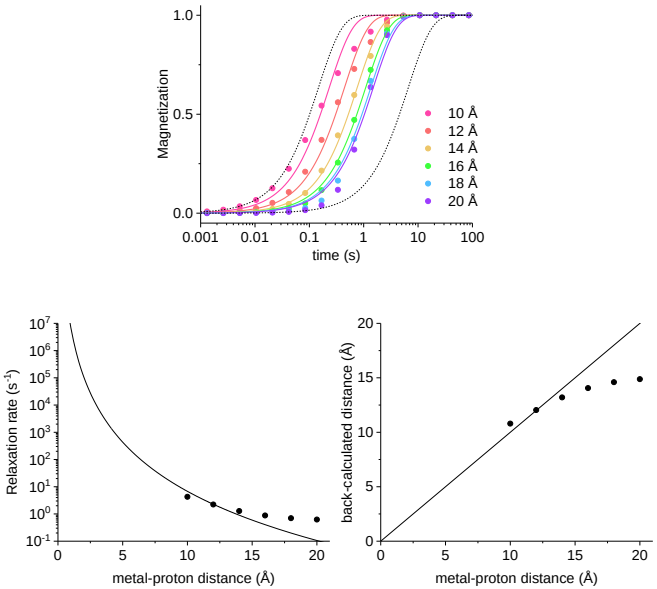

Figure S6. Calculated magnetization recovery for 6 protons placed along a straight line at 10, 12, 14, 16, 18 and 20 Å from a gadolinium ion, at 700 MHz (upper panel). The black dotted lines show the (monoexponential) behavior predicted from the Solomon equation for the two protons at 10 and 20 Å. The magnetization data calculated for the 6 protons are clearly not monoexponential. The monoexponential fits (solid colored lines) provide the relaxation rates and the back-calculated distances shown in the lower panels.

Fig. 1.

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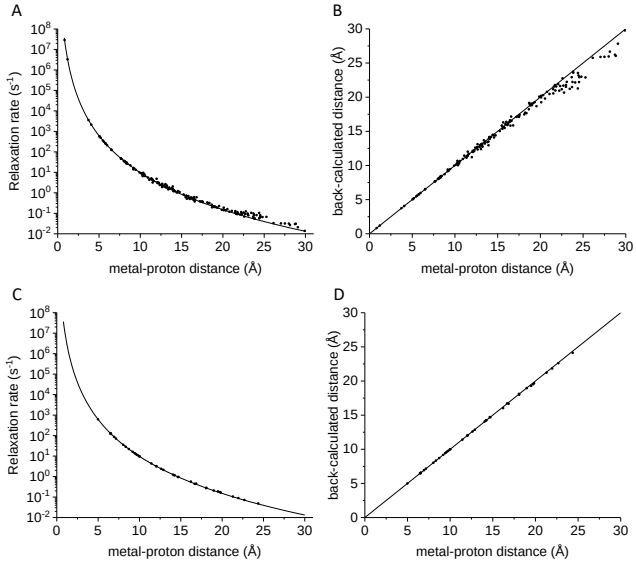

Figure S7. (A) Paramagnetic relaxation rates calculated at 500 MHz for Cu^{2+}-plastocyanin exchangeable (amide and hydroxyl) protons, in perdeuterated conditions. The line indicates the rates predicted with the Solomon equation. (C) Paramagnetic relaxation rates for isoleucine, leucine and valine methyl protons, assuming perdeuteration of all other hydrogens. (B and D) Agreement between metal-proton distances as measured in the PDB 2GIM structure and back-calculated from the predicted R_1 shown in panels A and C, respectively.

Fig. 2.

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