Your question to the audience
– a new concept of scientific contribution at the BeNeLux EPR society meetings

Henk Vrielinck <henk(dot)vrielinck(at)ugent(dot)be>

and Martina Huber <huber(at)physics(dot)leidenuniv(dot)nl>

In the 2023 meeting in Leiden, a new type of scientific contribution was launched. Since our community represents several decades of experience in EPR spectroscopy applied to a wide range of materials and application fields, questions currently encountered might have risen (and have found a solution) in the past. This is not always easily found back in the literature. Through this format of scientific discussion, we hope to help all reresearchers of our community in finding solutions to EPR-related problems of any kind they are struggling with.

The first edition of this type of presentation and discussion was kept modest, covering two questions, one from Ghent and one from Leiden University. The questions and proposed answers can be found in the subsequent pages of this document. The questions were presented by one person with the aid of a few slides in a few minutes. Afterwards ample time was given to the audience to react : ask further details about the question, acknowledge that similar problems have been encountered, propose solutions, explain why the problem is not easily solved, etc.

Even though it needs refinement, we are enthusiastic about further experimenting with this format of contributions in future EPR society meetings, in particular in the 2024 edition to be organized at Ghent University. In the feedback on the format during the "general meeting" at the end of the scientific meeting in 2023, it was suggested that the questions could be made available before the meeting, so that participants have the opportunity to prepare themselves. This and other suggestions that reach us will be considered seriously, also keeping in mind, of course, that the resulting format should not scare off possible presenters.

Any comments on this type of scientific discussion, suggestions on how we can improve it, and about the way we can communicate about it afterwards are welcome. They may be addressed to both Martina Huber and Henk Vrielinck (e-mails see higher in this document). This document can be considered dynamic, it will be updated based on reactions we receive. We sincerely hope that - with your help - this new presentation type will grow out to an integral scientific component of our meetings and prove to be very helpful to our community and to those who follow it (perhaps just from a distance).

December 2023

Henk Vrielinck (Chairman) and Martina Huber (Secretary)

Question 1: How to fit very broad EPR spectra (typical example, ferritin, FeOₓ)

Presenter: Jacqueline Labra Muñoz

Broad and featureless spectra, like the one of Ferritin (see Bossoni et al. Phys. Chem. Chem. Phys., 25, 27694–27717 (2023) do not lend themselves to automatic fitting. What we show is that a fit with two components, using a minimum set of parameters and a giant spin model approach gives physically

During the meeting

Questions: what is an appropriate spin Hamiltonian in such case?

Suggestion: probably this problem can only be solved if spectra are available under various experimental conditions, e.g. recorded at different microwave frequencies, different temperatures, etc.

Counter question: Is this not a classical example of an underdefined problem? One can construct a (complicated) spin Hamiltonian for it and fit its parameters, but the number of parameters in the model easily gets larger than the number of independent observations.

After the meeting

Martina Huber: there may be an approach suggested in the reference: Scientific Reports (2022) 12:3126 | https://doi.org/10.1038/s41598-022-07105-7

Fred Hagen, in response: In their theory, the FMR (equivalent to EPR) spectral shape is completely determined by the dimensions of a magnetite nanoparticle with a cigar (ellipsoid) shape, namely the two parameters: ratio of the semiaxes a/b of the ellipsoid, and transverse diameter D = 2b of the ellipsoid. The linewidth is determined by a third parameter, the magnetic damping constant kappa.

For fixed kappa the authors computer-generate 45 different spectra as a function of a/b and D. They then propose that we should fit experimental spectra as a linear combination of these 45 simulations.

Martina, I don't see how this could be of use for your ferritin problem. The spectral generator does not include any spin-Hamiltonian parameters, nor any electronic-structure parameters. What you don't put in, you can't get out. So there is no chemical information to be gained here. And the fitting procedure of experimental spectra is like a 'global analysis': you always get a good fit, but you don't really know what it means.
Martina: Indeed, I fully agree, my point was that one could take the inspiration, generate model spectra with one's model of choice and try the algorithm.

Bruker: I am not an expert on fitting very broad EPR signals, nor do I have much experience. With Aniso SpinFit it is possible to fit anisotropic and broad EPR spectra such as copper. Fitting of those spectra require the simulation of an anisotropic line broadening such as g-strain and A-strain. This is supported by Aniso SpinFit. If you have a single and "featureless" broad line, interpretation of the Aniso SpinFit result is of course difficult.
Answer (Martina): Interesting suggestion, I wonder if an S state of hundred could be tackled by SpinFit. Also, the fundamental problem of the spectrum having too few distinctive features is not addressed in the answer.

Question 2: How to find a good reference sample for quantifying paramagnetic species in a solid

Presenter: Henk Vrielinck – Ghent University

Typical "relatively easy" example goal: quantifying the concentration of color centers (electrons trapped at an anion vacancy) in complex oxide crystals

Typical "advanced/more difficult" example goal: quantifying the concentration of Gd^{3+} or Eu^{2+} in a complex oxide/halide

Context of the question: if one wants prove the involvement of paramagnetic centers in observed optical processes/effects, one very important and difficult to answer question is "do optical and paramagnetic centers occur in the same (similar) quantities?"

Reactions during the meeting

Reaction: for (relatively low) concentrations of complexes in solution the problem is "relatively easily" solved. A calibration curve can be constructed using known concentrations of the same or similarly behaving complexes in the same solution/solvent. E.g. for estimating the concentration of radical adduct concentrations to spin traps, a known procedure is to measure a (known) concentration series of TEMPO dissolved in the same solvent.

Reaction: for a solid the situation is way more complex. For a start, the measured and reference sample should exhibit the same (very similar) dielectric constant and dielectric losses.

After the meeting

Answer (Bruker): For quantification of CW-EPR data, our SpinCount accessory can be used. SpinCount (SC) is included in the Xepr, Xenon and Xenon_nano software suites. If you have a decent SNR, the accuracy of SpinCount is in our experience +/- 10%. A problem occurs when you have several paramagnetic components with spectral overlap. Then, SC will only yield the overall number of spins/concentration and not those of the individual components. A potential way out is to use our SpinFit modules (available for liquids and solids). If all components could be successfully fitted, SC can be applied to the fitted spectrum, and then you will of course get information about the individual components.

Quantification of pulse EPR data is not so straightforward. I know the Bode and Prisner lab have some publications on using the PELDOR background function to get information about the local concentration.