Notes on Thesis Corrections

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General

I have made some stylistic changes to the thesis (specifically, the formatting of the title page and chapter titles). Ralph asked about Oxford formatting guidelines. I am unaware of Oxford having specific thesis format guidelines, and haven't been able to find any guidance on this, so I am assuming that my thesis format is acceptable.

Spaces were added to between text and citations.

Corrections by page

Below is a list of corrections made which are not typo fixes. Text corrections have been highlighted in red.

Page 3 – Specified that only nuclei with odd numbers of protons and/or neutrons possess spin.

Page 3 – Mentioned molecular rotation as an additional source of angular momentum.

Page 3 – Equation 1.1: Squared the reduced Planck constant.

Page 3 – Replaced "with non-zero spin" with "with spin".

Page 4 – Table 1.1: Updated caption to include source of gyromagnetic ratios.

Page 4 – Replaced "which are spin-0" with "which do not possess spin".

Page 5 – Figure 1.1: Mentioned the sign of γ for each nucleus in the caption.

Page 6 – Mentioned that the high temperature approximation is applied in arriving at Equation 1.9b. See also **??**.

Page 7 – Re-worded description of RF pulse.

Page 8 – Equation 1.16: Corrected the expressions for $\tilde{\boldsymbol{i}}$ and $\tilde{\boldsymbol{j}}$.

Page 8 – Included a more detailed qualitative description of relaxation.

Page 11 – Explicitly mentioned the presence of a vacuum chamber.

Page 11 – Included solid-state NMR as an area that requires very high field strengths.

Page 11 – "inhomogeneities" → "small inhomogeneities".

Page 11 – A few extra details about the probe.

Page 12 – “is sent to” → “travels to”.

Page 13 – Peter suggested that I mention how data could be treated if there were lineshape distortions (annotation on Section 3.1.2 heading). Footnote ** mentions reference deconvolution as a means of correcting these in order to yield Lorentzian lineshapes.

Page 12 – Replace “sweep width” with “spectral width”. This has been done in numerous places in the thesis.

Page 13 – Equation 1.21b: Correct equation label.

Page 17 – Mentioned that exponential broadening is not the optimal window function for sensitivity enhancement. See also Footnote ‡‡.

Page 17 – Improved comparison of Gaussian vs Lorentzian lineshapes.

Page 18 – Reworded paragraph on truncation artefacts.

Page 18 – Elaborated on Kramers-Kronig relations, and included a citation.

Page 19 – Added Footnote ¶¶ to mention the lock’s use of dispersion lineshapes for monitoring field drifts.

Page 22 – Removed footnote discussing consideration of linewidth for T_2 measurement, as this is not reliable.

Page 26 – Ralph commented that iterative methods are employed routinely in ^{13}C NMR for metabolomics fingerprinting. I am unaware of this; from what I am aware, the typical method of performing metabolomics fingerprinting is to break up spectrum into small regions (bins), integrate these bins, and then input the integrals into some routine for multivariate analysis, such as PCA. I have added the phrase “like VARPRO and AMARES” to clarify what I mean by an “iterative method”.

Page 27 – Improved wording of why holistically analysing a 2D dataset can be better than sequentially analysing 1D increments.

Page 31 – Added citations to make the fact that the routine makes use of previous theory more explicit.

Page 32 – Peter mentioned that a square root was absent in the probability density (what was Equation 2.3 in my pre-viva draft). The square root wasn’t present as the expression was the product of the PDFs of the real and imaginary components of a particular datapoint. I have rewritten this to make the origin of the scaling factor more clear.

Page 34 – Added Footnote † to give the definition of a matrix pencil.

Page 51 – AWGN is referred to only the first time it is added to simulated data; after this, I simply refer to it as “noise”. See also Remark 2, Page 51.

Page 54 – Added Footnote ¶¶ to provide a bit more context on why 25 was chosen as the number of iterations between negative amplitude checks.

Page 55 – Brief discussion about limitations on FID size, based on RAM requirements, in the context of Pines' 1997 paper on the MPM.

Page 56 – Figure 2.4: Made caption and y-axis texts equivalent. Indicated where $96MiB$ appears on the MPM peak memory usage plot, to help with the 1997 paper discussion.

Page 61 Tweak to the first sentences in Section 2.5 to emphasise that NMR users are unlikely to use software if it takes a long time to run.

Page 63 – Mentioned that the filtering process could likely be replaced by the simpler method of using a rectangular filter and slicing at the filter boundaries.

Page 70 – Mentioned that timings for 1D estimation are available in the new Table C.7 (Page 191).

Page 71 – Figure 3.1: Replaced landscape figure with portrait version. Included a description of the different peak colours in the caption.

Page 73 – Added Footnote $*$ to provide some additional context to the phase "similar frequencies".

Page 77 – Mentioned that a possible approach to under-fitting is to "split" oscillators in the parameter estimate and re-optimise; discussed limitations associated with this.

Page 77 Noted that even when a parsimonious fit occurred for spin (O), certain parameters are not perfectly consistent with expectations (i.e. amplitudes are not exactly equal).

Page 74 – Figure 3.2: Replaced landscape figure with portrait version. Added structure of andrographolide.

Page 78 – Figure 3.3: Added structure of cyclosporin, and edited the caption accordingly.

Page 79 – Replaced "the spin tumbles" with "the molecule that the spin is associated with tumbles".

Page 80 – Discussed issues with chemical shift evolution if naïve 90° – delay – detect experiment were used for T_2 determination.

Page 82 – Corrected the definition for diffusion time Δ.

Page 82 – Figure 3.4: Tweaked the relative widths of pulses and gradients.

Page 83 – $T_1 \ll T_2 \rightarrow T_1 \gg T_2$.

Page 83 – "It is virtually always the case that FID's signal amplitudes will abide by the following general form of the Stejskal-Tanner equation, regardless of the exact pulse sequence used:" → "The FID's signal amplitudes always abide by the following general form of the Stejskal-Tanner equation, regardless of the exact pulse sequence used:". Ralph queried whether I knew of any diffusion experiments which are exceptions to the equation I provide; I do not, so have changed the text accordingly.

Page 83 – Fixed unit of constant c in Stejskal-Tanner.

Page 90 – Provided an explicit expression for the errors associated with D, T_1, T_2 measurements. A derivation of a similar expression for FID parameter estimate errors is given in the appendix.

Page 91 – Figure 3.5: Edited panel d; changed the aspect ratio and viewing angle. Hopefully the lineshapes look better with the altered view. If you still think it looks odd, I could simply remove the panel altogether; it is not the most crucial aspect of the figure, though I think it is nice to give the reader an idea of how the oscillators vary across increments.

Page 93 – Figure 3.6: Replaced landscape figure with portrait version. Added structure of andrographolide.

Page 94 – Figure 3.7: Added structures of valine, threonine and major anomeric forms of glucose.

Page 95 – Brief mention of likely cause for difference in diffusion constants between glucose anomers.

Page 96 – Added references to optimal control pulses for broadband excitation.

Page 97 – Figure 3.8: Explicitly stated that the flip angle of the chirp pulse is 90° in the caption.

Page 100 – Included a discussion of how J-couplings may influence the efficacy of the method.

Page 99 – Figure 3.9: Made explicit reference to baseline distortions in panel b.

Page 100 – Improved description of Gd-doped sample. See also the caption of Figure 3.10.

Page 101 – Figure 3.10: Provided a description of the experiment used to generate the dataset in the caption.

Page 102 – Reworded a sentence in the summary.

Page 103 – Peter queried my statement that data sensitivity is proportional to $\sqrt{\mathrm{NS}}$. I believe this to be correct; when the number of scans is quadrupled, a doubling in sensitivity is expected.

Page 105 – Provided further discussion of strong coupling artefacts in 2DJ NMR. Added a detailed account of the form of a dataset produced by an AB spin system (see also the new Figure 4.1), and a mention that aliasing of strong coupling artefacts in the indirect dimension is common.

Page 111 – Separated discussions for using PSYCHE in a Keeler-Pell-style experiment, and PSYCHE-2DJ.

Page 116 Clarified that CUPID does not directly produce coupling constant predictions.

Page 119 – Figure 4.7: Added structure of strychnine.

Page 120 – Figure 4.8: Added structure of quinine.

Page 122 – Figure 4.9: Added structure of camphor. Included a description of grey points in the figure.

Page 124 – Figure 4.10: Replaced landscape figure with portrait version. Added structure of dexamethaone. Included a description of grey points in the figure.

Page 125 – Figure 4.11: Added structure of estradiol. Included a description of grey points in the figure.

Page 126 – Enumerated the steps that a user must undertake to use CUPID.

Page 140 – Added a discussion on how multiprocessing could be employed to improve the efficiency of NMR-EsPy.

Page 190 – Figure C.3: Removed excessive number of gradient recovery delays in TSE-PSYCHE pulse sequence.