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~~Data Processing and~~ Peak Integration Methods in qNMR

qNMR Day — Bari, Italy

Mike Bernstein 24th November, 2017

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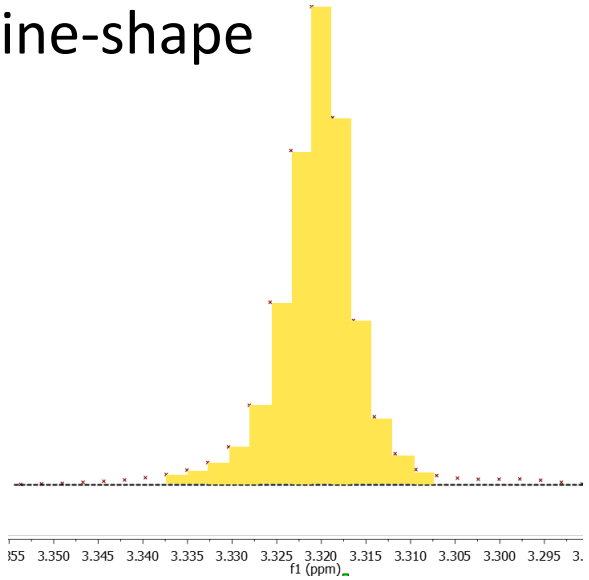
"Sum" integration – the good

- Universally accepted, works well
- Simple calculation
- Insensitive to line-shape



- Good-excellent phase- and baseline corrections
- Adequate data density needed
- Signal-intense regions
- Must integrate the *entire* signal(s)
- Signal overlap can be an issue

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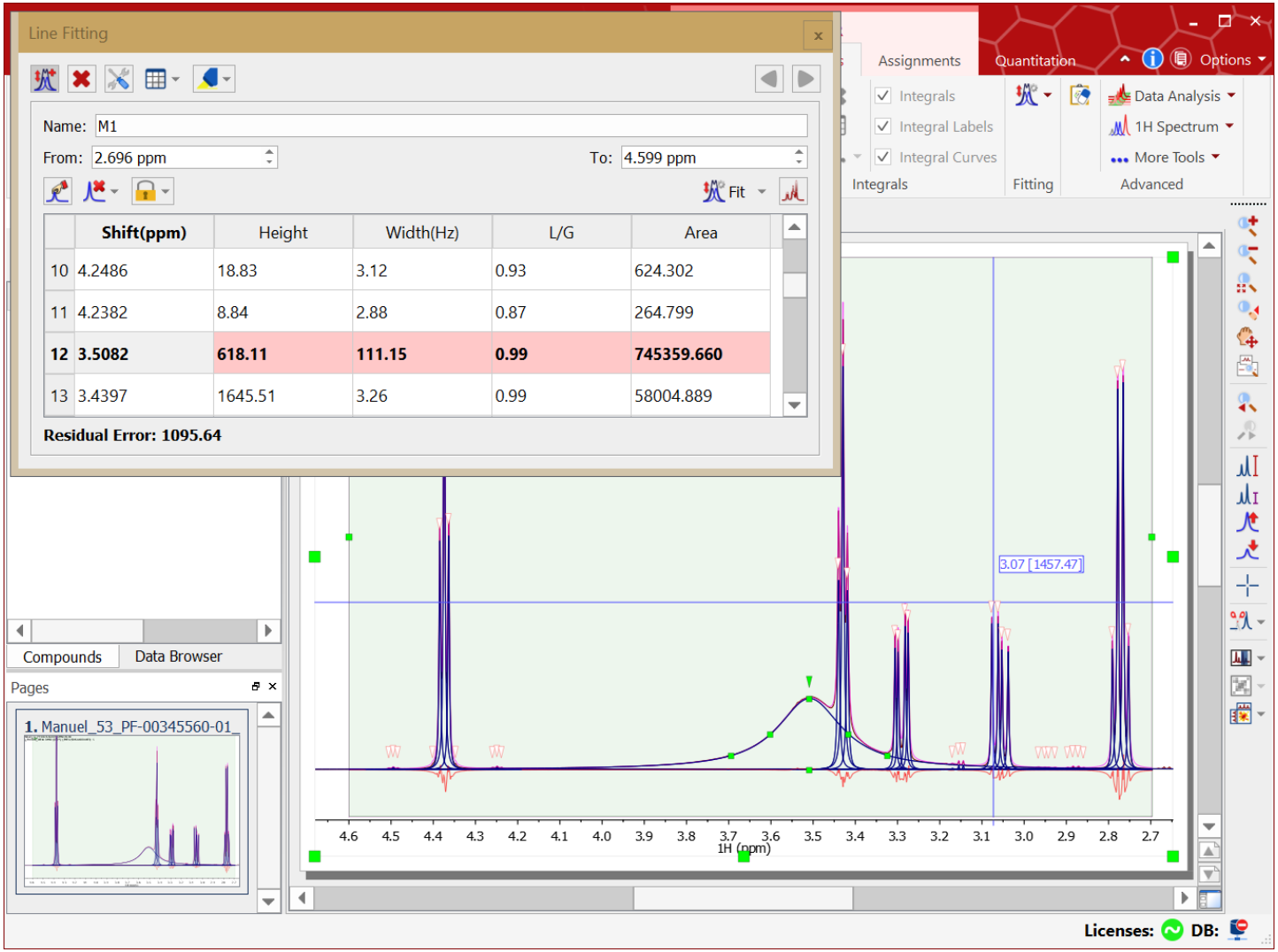
Peak deconvolution

Independent areas of (all) peaks in the spectrum

Time- or frequency domain calculation



	Shift(ppm)	Height	Width(Hz)	L/G	Area
10	4.2486	18.83	3.12	0.93	624.302
11	4.2382	8.84	2.88	0.87	264.799
12	**3.5082**	**618.11**	**111.15**	**0.99**	**745359.660**
13	3.4397	1645.51	3.26	0.99	58004.889

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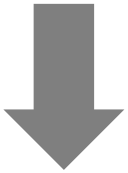
Global Spectrum Deconvolution (GSD)

Automatic multiplet deconvolution of the whole spectrum to recognize and extract all peaks, and discard artefacts

- ❑ Recognition of all significant peaks before fitting
- ❑ Assignment of realistic *a priori* bounds to peak parameters
- ❑ Fitting of hundreds of parameters in a reasonable time

- ❑ List of peaks (centre, height, width, phase, shape)
- ❑ Synthetic spectrum
- ❑ Array of residues



Integral of each peak

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GSD → *values* representing the *real spectrum*

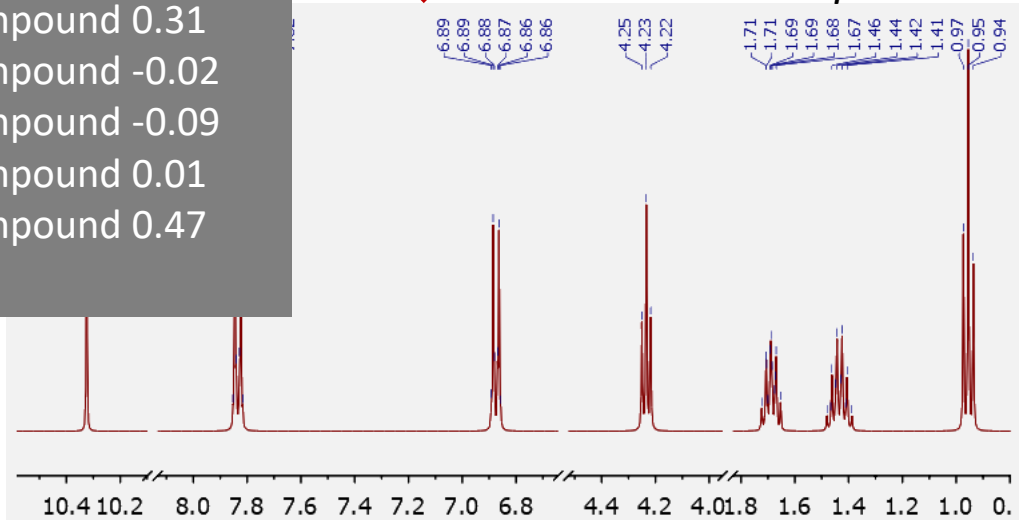
Name	Shift	H's	Integral
A (s)	10.32	1	0.901
B (m)	7.83	2	2.045
C (m)	6.87	2	1.964
D (t)	4.23	2	2.000
E (m)	1.69	2	1.907
F (m)	1.44	2	2.054
G (t)	0.95	3	2.841

Multiplets

Ppm	Intensity	Width	Area	Type	Kurtosis
10.32	0.1	1.17	2.72	Compound	0.62
7.85	0.0	1.29	0.16	Compound	-0.20
7.85	0.1	1.43	2.34	Compound	0.08
7.84	0.0	1.36	0.52	Compound	-0.16
7.83	0.0	1.51	0.63	Compound	0.29
7.82	0.1	1.39	2.41	Compound	0.14
7.82	0.0	1.05	0.12	Compound	0.80
6.89	0.0	1.13	0.20	Compound	0.16
6.89	0.1	1.33	2.27	Compound	0.31
6.88	0.0	1.27	0.53	Compound	-0.02
6.87	0.0	1.31	0.63	Compound	-0.09
6.86	0.1	1.28	2.20	Compound	0.01
6.86	0.0	0.96	0.11	Compound	0.47
…					

Experimental spectrum

Synthetic spectrum



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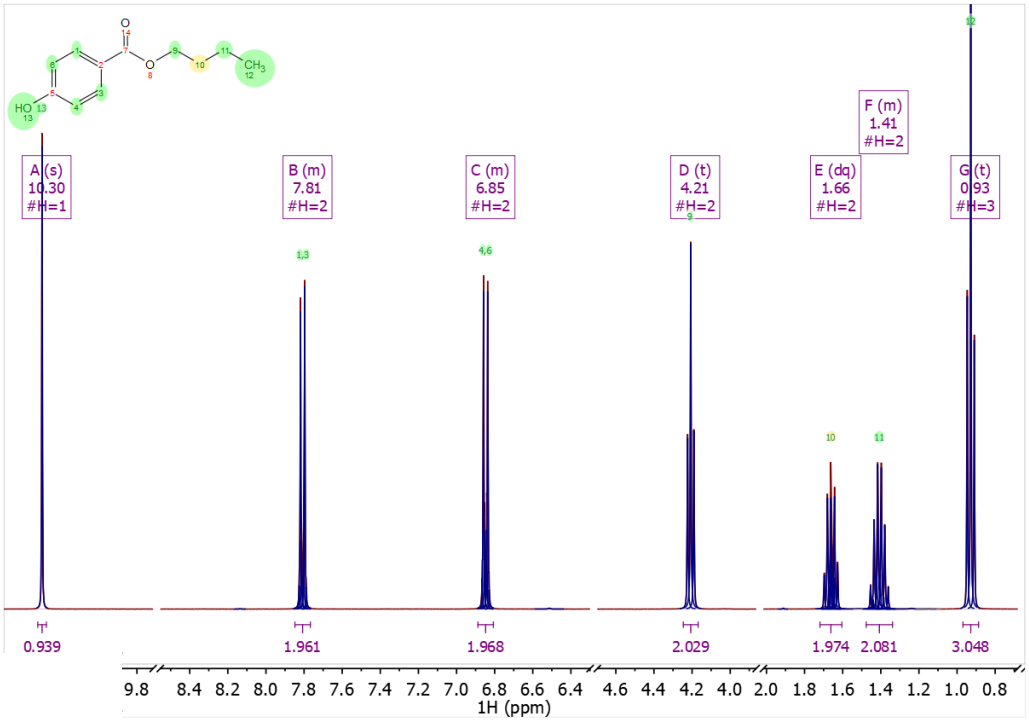
Integration performance



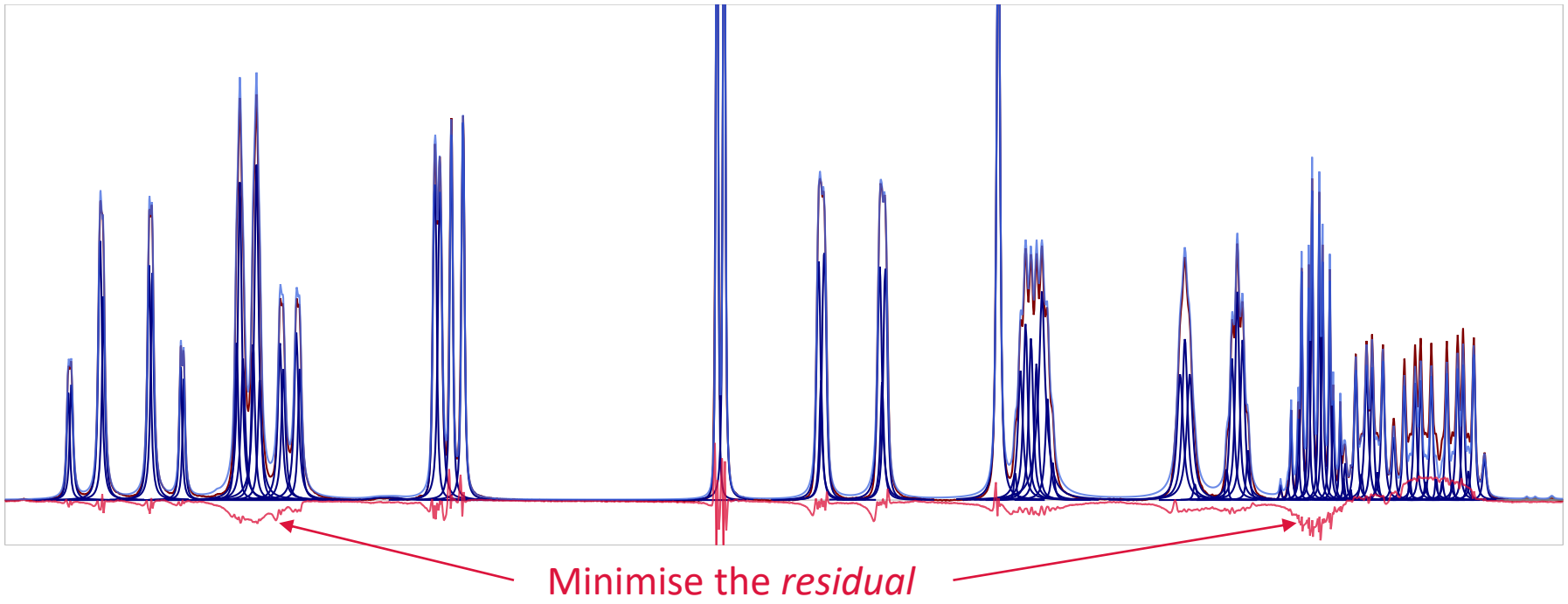
	Sum		GSD		
Shift (ppm)	Abs	Abs/H	Abs	Abs/H	
0.93	8.240	2.747	9.050	3.017	
1.41	5.540	2.770	6.180	3.090	
1.66	5.490	2.745	5.860	2.930	
4.21	5.490	2.745	6.030	3.015	
6.85	5.500	2.750	5.850	2.925	
7.81	5.490	2.745	5.830	2.915	
10.3	2.670	2.670	2.790	2.790	
		2.7388		2.9545	Ave
		1.16		3.27	RSD%

N.B.

Improving GSD for qNMR

Problem: experimental peak shapes often deviate from ideal models like a generalised Lorentzian.

Approach: increasingly add more adjustment parameters to the models till it represent the experimental shapes better. The quality is judged by analysis of remaining residuals. Can be done in multiple cycles.



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Improving peak fitting: Managing residuals

2014 IEEE International Conference on Acoustic, Speech and Signal Processing (ICASSP)

EFFICIENT PEAK EXTRACTION OF PROTON NMR SPECTROSCOPY USING LINESHAPE ADAPTATION

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"The method is an iterative process where the largest peak is estimated and removed from the spectrum which then uncovers the smaller peaks."

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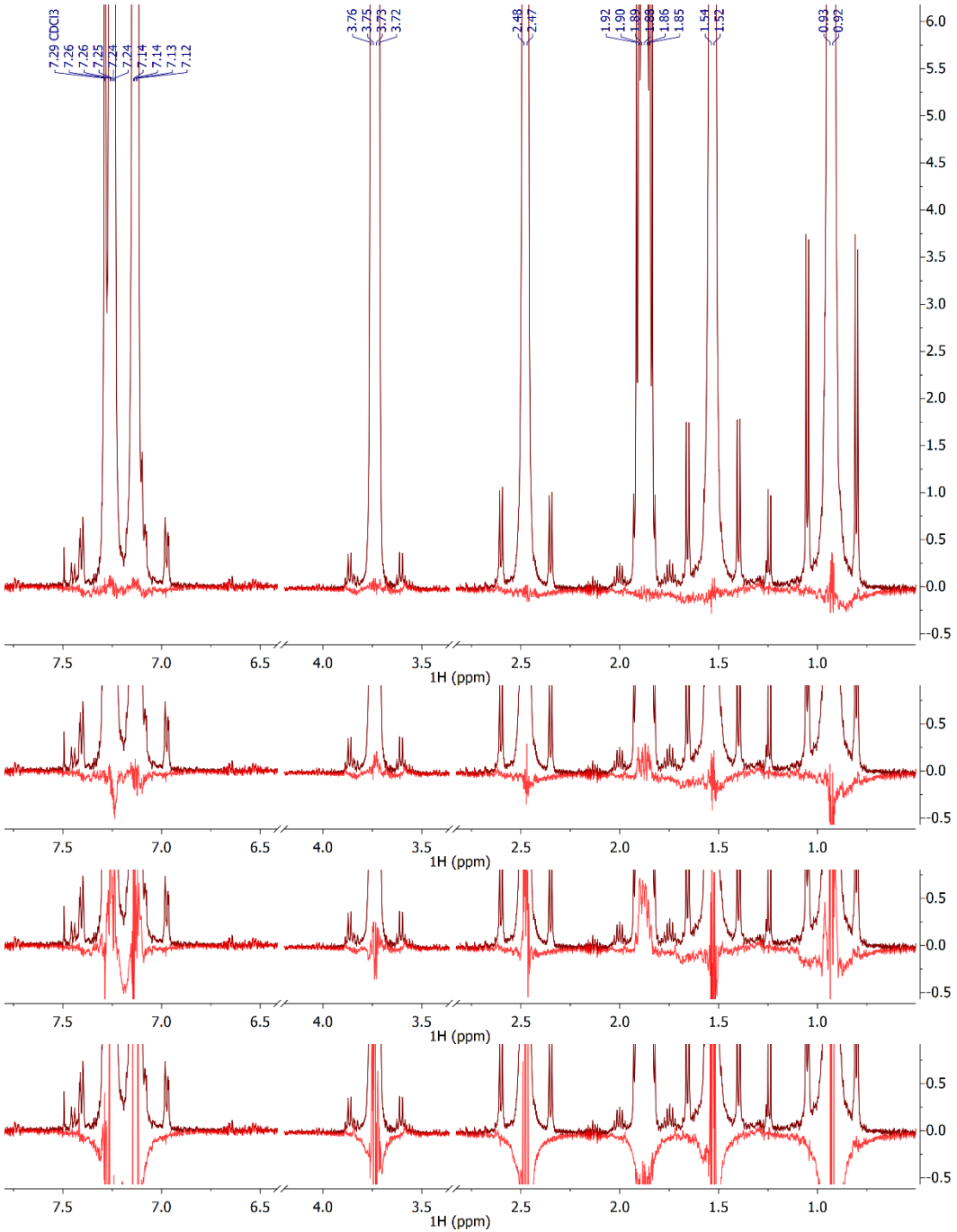
qGSD Iterative improvement

6

4

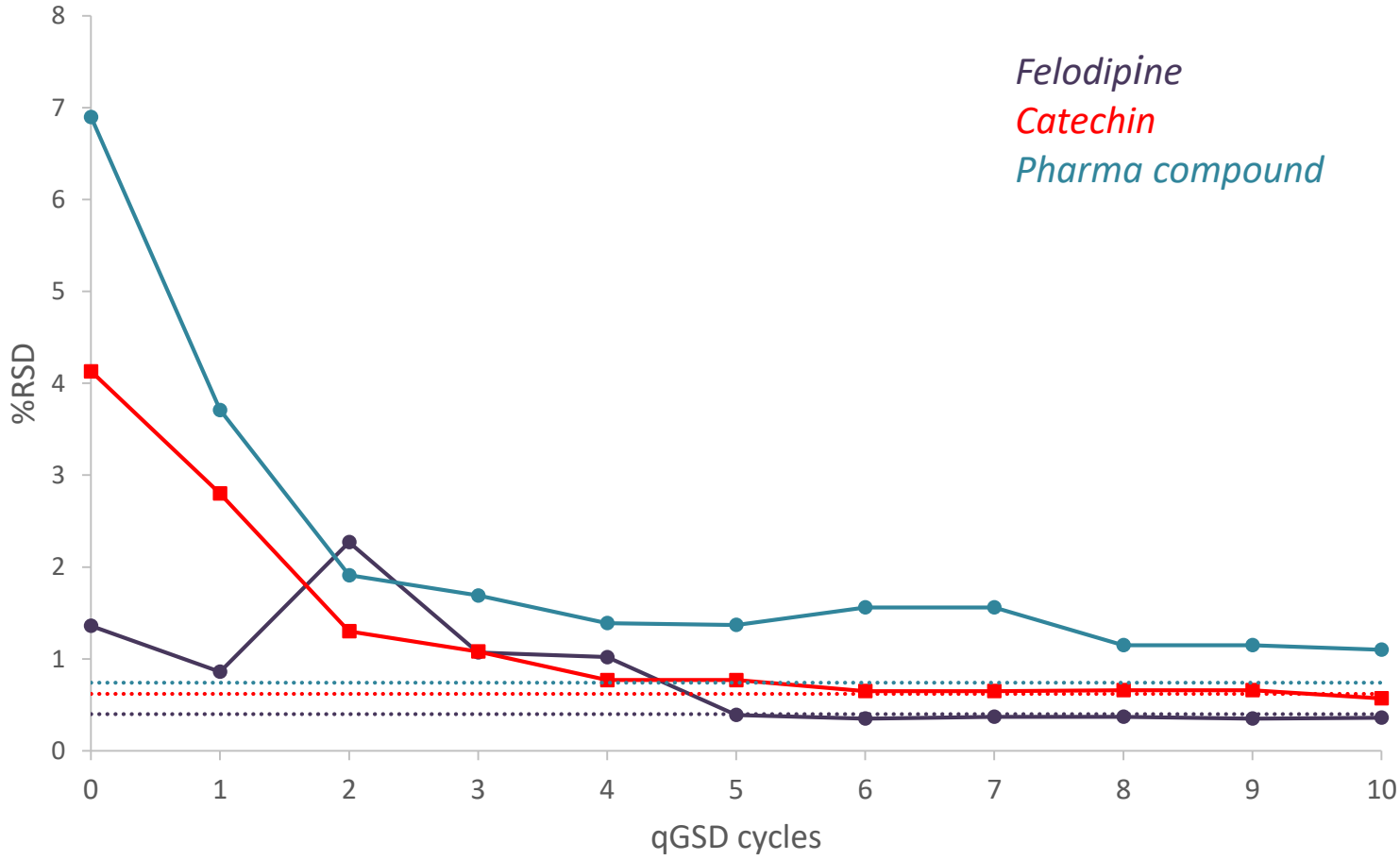
2

qGSD iterations: 0



qGSD - convergence

qGSD integration RMSD% as a function of the number of improvement cycles.
Dotted lines of the matching colour shows the RSD values of the sum integration



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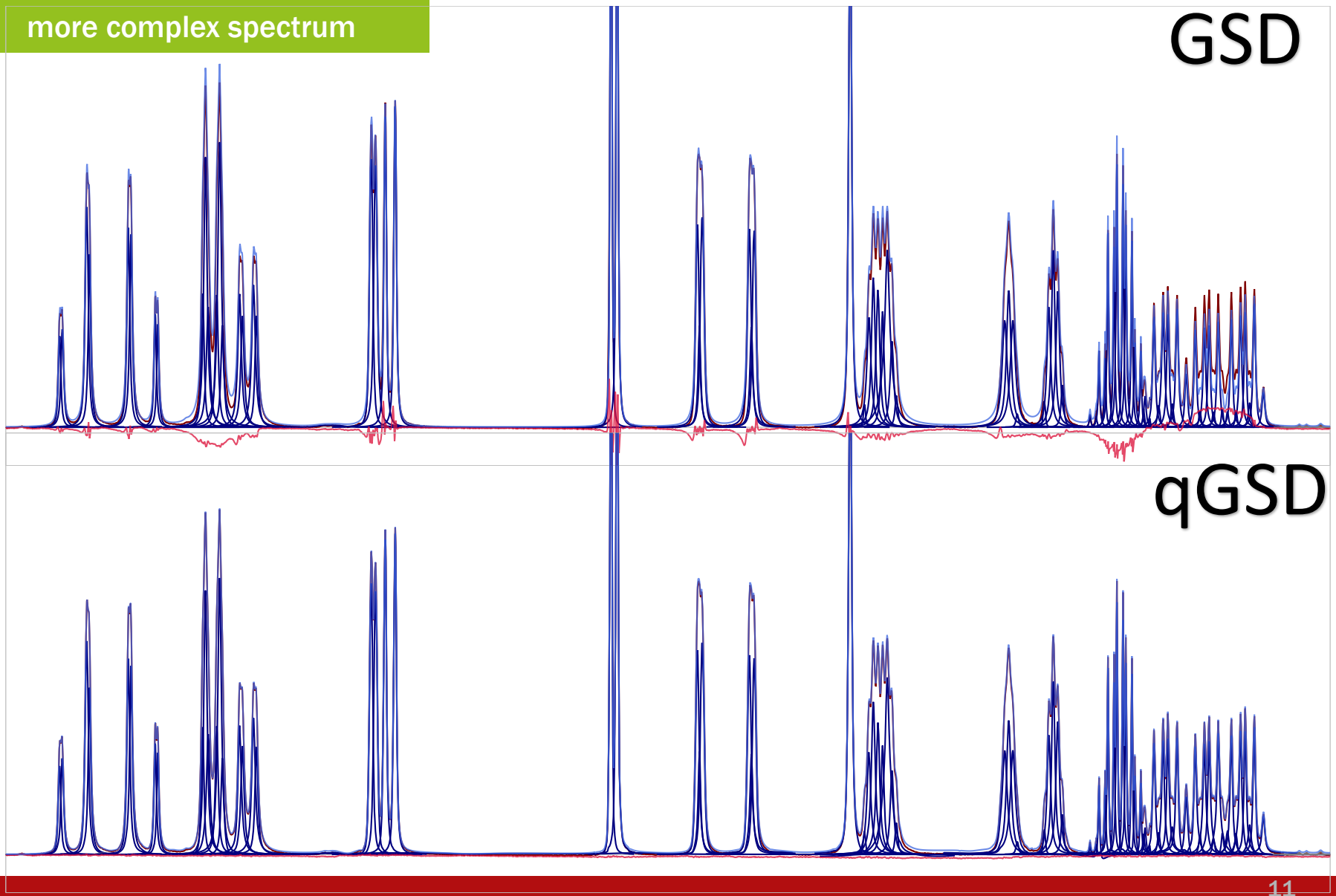
GSD/qGSD –
more complex spectrum



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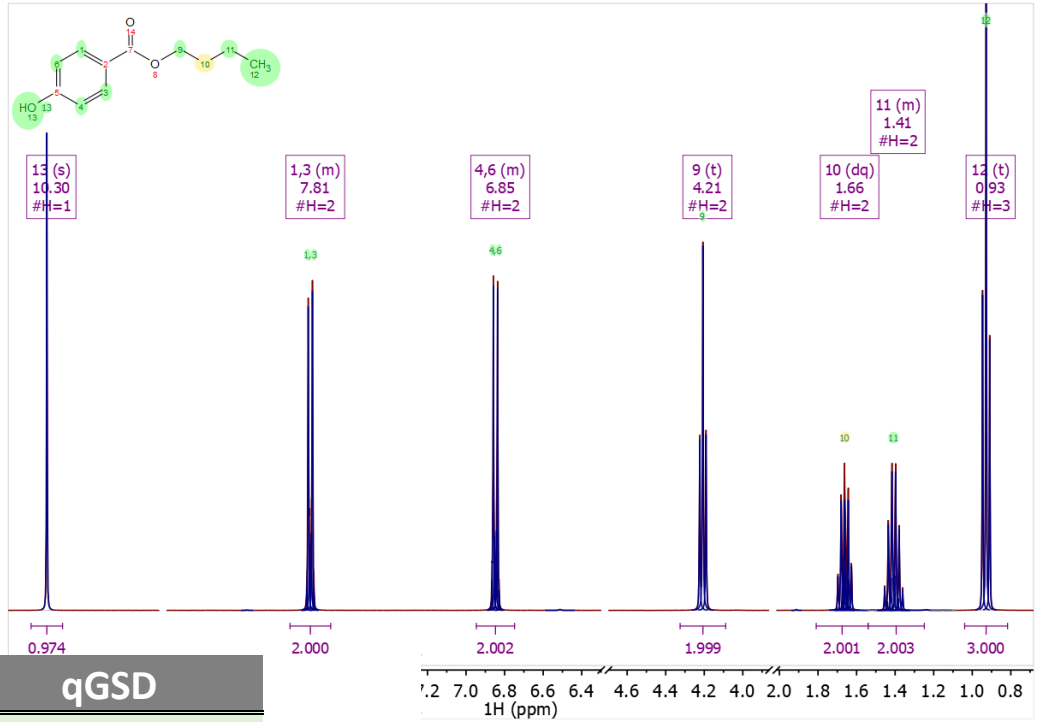
Integration performance



	Sum		GSD		qGSD		
Shift (ppm)	Abs	Abs/H	Abs	Abs/H	Abs	Abs/H	
0.93	8.240	2.747	9.050	3.017	8.230	2.743	
1.41	5.540	2.770	6.180	3.090	5.500	2.750	
1.66	5.490	2.745	5.860	2.930	5.490	2.745	
4.21	5.490	2.745	6.030	3.015	5.480	2.740	
6.85	5.500	2.750	5.850	2.925	5.490	2.745	
7.81	5.490	2.745	5.830	2.915	5.490	2.745	
10.3	2.670	2.670	2.790	2.790	2.670	2.670	
		2.7388		2.9545		2.734	Ave
		1.16		3.27		1.04	RSD%

N.B.

Conclusions

qNMR integration can be accomplished under a wide range of conditions

Sum integration may be the gold standard, but is not always practically applicable

Deconvolution techniques, e.g., GSD, can be used when peaks are close or overlap

Improved GSD, qGSD, accounts for excellent deconvolution of “real world” peaks

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