

relax

Version 3.0.2



**Molecular dynamics by
NMR data analysis**

November 26, 2013

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Abbreviations

AIC: Akaike's Information Criteria (model selection method)

AICc: small sample size corrected AIC (model selection method)

API: application programming interface

ANOVA: analysis of variance (field of statistics)

BIC: Bayesian Information Criteria (model selection method)

BFGS: Broyden-Fletcher-Goldfarb-Shanno (optimisation method)

$C(\tau)$: correlation function

χ^2 : chi-squared function

CG: conjugate gradient (optimisation)

CSA: chemical shift anisotropy

CV: cross validation

CVS: Concurrent Versions System (open source version control system)

\mathfrak{D} : the set of diffusion tensor parameters

\mathfrak{D}_{\parallel} : the eigenvalue of the spheroid diffusion tensor corresponding to the unique axis of the tensor

\mathfrak{D}_{\perp} : the eigenvalue of the spheroid diffusion tensor corresponding to the two axes perpendicular to the unique axis

\mathfrak{D}_a : the anisotropic component of the Brownian rotational diffusion tensor

\mathfrak{D}_{iso} : the isotropic component of the Brownian rotational diffusion tensor

\mathfrak{D}_r : the rhombic component of the Brownian rotational diffusion tensor

\mathfrak{D}_{ratio} : the ratio of \mathfrak{D}_{\parallel} to \mathfrak{D}_{\perp}

\mathfrak{D}_x : the eigenvalue of the Brownian rotational diffusion tensor in which the corresponding eigenvector defines the x-axis of the tensor

\mathfrak{D}_y : the eigenvalue of the Brownian rotational diffusion tensor in which the corresponding eigenvector defines the y-axis of the tensor

- \mathfrak{D}_z :** the eigenvalue of the Brownian rotational diffusion tensor in which the corresponding eigenvector defines the z-axis of the tensor
- ϵ_i : elimination value
- FSF:** Free Software Foundation
- GNU:** GNU's Not Unix!
- PGP:** GNU Privacy Guard (software)
- GPL:** GNU general public licence
- GUI:** graphical user interface
- ID string:** identification string
- $J(\omega)$: spectral density function
- MC:** Monte Carlo (simulations)
- MD:** molecular dynamics (simulations)
- MPI:** message passing interface
- NMR:** if you do not know this one, do not read further
- NNTP:** network news transfer protocol
- NOE:** nuclear Overhauser effect
- ORD:** optical rotatory dispersion
- OS:** operating system
- PCS:** pseudocontact shift
- PDB:** Protein Data Bank
- pdf:** probability distribution function
- PRE:** paramagnetic relaxation enhancement
- r : bond length
- R_1 : spin-lattice relaxation rate
- R_2 : spin-spin relaxation rate
- R_{ex} : chemical exchange relaxation rate
- RDC:** residual dipolar coupling
- RMSD:** root-mean-square deviation
- ROE:** rotating-frame Overhauser effect
- RSDM:** reduced spectral density mapping
- RSS:** rich site summary (web feed format)

S^2 , S_f^2 , and S_s^2 : model-free generalised order parameters

SVN: Apache Subversion (open source version control system)

τ_e , τ_f , and τ_s : model-free effective internal correlation times

τ_m : global rotational correlation time

UI: user interface

XML: extensible markup language

Preface - citing relax

The relax project is a large collection of work created by diverse authors. It is a community driven project created by NMR spectroscopists which supports a broad range of dynamics analyses. Care must be taken to properly cite the parts of relax that you use so that the correct authors receive the citations and credit they deserve. The following is a breakdown of all of the citations relating to relax, including the basic citations for the various analysis types.

The software relax

relax references

The primary citations for relax are:

- d'Auvergne, E. J. and Gooley, P. R. (2008a). Optimisation of NMR dynamic models I. Minimisation algorithms and their performance within the model-free and Brownian rotational diffusion spaces. *J. Biomol. NMR*, **40**(2), 107–119. ([10.1007/s10858-007-9214-2](https://doi.org/10.1007/s10858-007-9214-2))
- d'Auvergne, E. J. and Gooley, P. R. (2008b). Optimisation of NMR dynamic models II. A new methodology for the dual optimisation of the model-free parameters and the Brownian rotational diffusion tensor. *J. Biomol. NMR*, **40**(2), 121–133. ([10.1007/s10858-007-9213-3](https://doi.org/10.1007/s10858-007-9213-3))

Graphical user interface reference

The primary citation for the GUI is:

- Bieri, M., dAuvergne, E., and Gooley, P. (2011). relaxGUI: a new software for fast and simple NMR relaxation data analysis and calculation of ps-ns and μ s motion of proteins. *J. Biomol. NMR*, **50**, 147–155. ([10.1007/s10858-011-9509-1](https://doi.org/10.1007/s10858-011-9509-1))

The multi-processor reference

Although not published, if the multi-processor framework is used to run relax on multi-core systems, grids, or clusters, then please acknowledge the author of that code – Gary Thompson.

Specific analyses

The following subsections list the citations for the individual analysis specific parts of relax.

Model-free analysis references

The base citations for model-free theory are:

- Lipari, G. and Szabo, A. (1982a). Model-free approach to the interpretation of nuclear magnetic-resonance relaxation in macromolecules I. Theory and range of validity. *J. Am. Chem. Soc.*, **104**(17), 4546–4559. ([10.1021/ja00381a009](https://doi.org/10.1021/ja00381a009))
- Lipari, G. and Szabo, A. (1982b). Model-free approach to the interpretation of nuclear magnetic-resonance relaxation in macromolecules II. Analysis of experimental results. *J. Am. Chem. Soc.*, **104**(17), 4559–4570. ([10.1021/ja00381a010](https://doi.org/10.1021/ja00381a010))
- Clore, G. M., Szabo, A., Bax, A., Kay, L. E., Driscoll, P. C., and Gronenborn, A. M. (1990). Deviations from the simple 2-parameter model-free approach to the interpretation of N-15 nuclear magnetic-relaxation of proteins. *J. Am. Chem. Soc.*, **112**(12), 4989–4991. ([10.1021/ja00168a070](https://doi.org/10.1021/ja00168a070))

If the automated analysis of the `dauvergne_protocol.py` sample script or the GUI model-free analysis which uses the same protocol has been used, then the following citations are all implicit:

- d'Auvergne, E. J. and Gooley, P. R. (2003). The use of model selection in the model-free analysis of protein dynamics. *J. Biomol. NMR*, **25**(1), 25–39. ([10.1023/a:1021902006114](https://doi.org/10.1023/a:1021902006114))
- d'Auvergne, E. J. and Gooley, P. R. (2006). Model-free model elimination: A new step in the model-free dynamic analysis of NMR relaxation data. *J. Biomol. NMR*, **35**(2), 117–135. ([10.1007/s10858-006-9007-z](https://doi.org/10.1007/s10858-006-9007-z))
- d'Auvergne, E. J. and Gooley, P. R. (2007). Set theory formulation of the model-free problem and the diffusion seeded model-free paradigm. *Mol. BioSyst.*, **3**(7), 483–494. ([10.1039/b702202f](https://doi.org/10.1039/b702202f))
- d'Auvergne, E. J. and Gooley, P. R. (2008a). Optimisation of NMR dynamic models I. Minimisation algorithms and their performance within the model-free and Brownian rotational diffusion spaces. *J. Biomol. NMR*, **40**(2), 107–119. ([10.1007/s10858-007-9214-2](https://doi.org/10.1007/s10858-007-9214-2))

- d'Auvergne, E. J. and Gooley, P. R. (2008b). Optimisation of NMR dynamic models II. A new methodology for the dual optimisation of the model-free parameters and the Brownian rotational diffusion tensor. *J. Biomol. NMR*, **40**(2), 121–133. ([10.1007/s10858-007-9213-3](https://doi.org/10.1007/s10858-007-9213-3))

Otherwise, if model-free analysis is used in relax but not via the inbuilt automated protocol, the first reference is for model selection, the second is for eliminating failed model-free models, and the forth is for the optimisation improvements (the third and fifth are for the automated protocol). All of the model-free implementation details of relax are covered by the PhD thesis (available as a PDF or as a printed version on Amazon.com) of:

- d'Auvergne, E. J. (2006). *Protein dynamics: a study of the model-free analysis of NMR relaxation data*. PhD thesis, Biochemistry and Molecular Biology, University of Melbourne. <http://eprints.infodiv.unimelb.edu.au/archive/00002799/>. ([10.187/2281](https://doi.org/10.187/2281))

The reference for the hybridisation of different global diffusion models to analyse the residual inter-domain dynamics – a not very well documented feature of relax – is:

- Horne, J., d'Auvergne, E., Coles, M., Velkov, T., Chin, Y., Charman, W., Prankerd, R., Gooley, P., and Scanlon, M. (2007). Probing the flexibility of the DsbA oxidoreductase from *Vibrio cholerae*—a ¹⁵N - ¹H heteronuclear NMR relaxation analysis of oxidized and reduced forms of DsbA. *J. Mol. Biol.*, **371**(3), 703–716. ([10.1016/j.jmb.2007.05.067](https://doi.org/10.1016/j.jmb.2007.05.067))

If the software Modelfree4 or Dasha are used as replacement optimisation engines from within relax, the citations for Modelfree4 are:

- Palmer, A. G., Rance, M., and Wright, P. E. (1991). Intramolecular motions of a zinc finger DNA-binding domain from Xfin characterized by proton-detected natural abundance C-12 heteronuclear NMR-spectroscopy. *J. Am. Chem. Soc.*, **113**(12), 4371–4380. ([10.1021/ja00012a001](https://doi.org/10.1021/ja00012a001))
- Mandel, A. M., Akke, M., and Palmer, 3rd, A. G. (1995). Backbone dynamics of *escherichia coli* ribonuclease HI: correlations with structure and function in an active enzyme. *J. Mol. Biol.*, **246**(1), 144–163. ([10.1006/jmbi.1994.0073](https://doi.org/10.1006/jmbi.1994.0073))

and for Dasha:

- Orekhov, V. Y., Nolde, D. E., Golovanov, A. P., Korzhnev, D. M., and Arseniev, A. S. (1995a). Processing of heteronuclear NMR relaxation data with the new software DASHA. *Appl. Magn. Reson.*, **9**(4), 581–588. ([10.1007/bf03162365](https://doi.org/10.1007/bf03162365))

Consistency testing analysis references

The base citations for the consistency testing of NMR relaxation is:

- Fushman, D., Tjandra, N., and Cowburn, D. (1999). An approach to direct determination of protein dynamics from ^{15}N NMR relaxation at multiple fields, independent of variable ^{15}N chemical shift anisotropy and chemical exchange contributions. *J. Am. Chem. Soc.*, **121**(37), 8577–8582. ([10.1021/ja9904991](https://doi.org/10.1021/ja9904991))
- Farrow, N. A., Zhang, O. W., Szabo, A., Torchia, D. A., and Kay, L. E. (1995). Spectral density-function mapping using N-15 relaxation data exclusively. *J. Biomol. NMR*, **6**(2), 153–162. ([10.1007/bf00211779](https://doi.org/10.1007/bf00211779))
- Fushman, D., Tjandra, N., and Cowburn, D. (1998). Direct measurement of ^{15}N chemical shift anisotropy in solution. *J. Am. Chem. Soc.*, **120**(42), 10947–10952. ([10.1021/ja981686m](https://doi.org/10.1021/ja981686m))

The first is the main citation, whereas the next are the individual tests. The citation for the consistency testing of NMR relaxation as implemented in relax is:

- Morin, S. and Gagné, S. (2009a). Simple tests for the validation of multiple field spin relaxation data. *J. Biomol. NMR*, **45**, 361–372. ([10.1007/s10858-009-9381-4](https://doi.org/10.1007/s10858-009-9381-4))

N-state model analysis references

Some citations demonstrating as well as presenting the use of the N-state model for diverse analyses types are:

- Sun, H., d'Auvergne, E. J., Reinscheid, U. M., Dias, L. C., Andrade, C. K. Z., Rocha, R. O., and Griesinger, C. (2011). Bijvoet in solution reveals unexpected stereoselectivity in a michael addition. *Chem. Eur. J.*, **17**(6), 1811–1817. ([10.1002/chem.201002520](https://doi.org/10.1002/chem.201002520))
- Erdelyi, M., d'Auvergne, E., Navarro-Vazquez, A., Leonov, A., and Griesinger, C. (2011). Dynamics of the glycosidic bond: Conformational space of lactose. *Chem. Eur. J.*, **17**(34), 9368–9376. ([10.1002/chem.201100854](https://doi.org/10.1002/chem.201100854))

Reduced spectral density mapping references

The base citations for reduced spectral density mapping are:

- Farrow, N. A., Zhang, O. W., Szabo, A., Torchia, D. A., and Kay, L. E. (1995). Spectral density-function mapping using N-15 relaxation data exclusively. *J. Biomol. NMR*, **6**(2), 153–162. ([10.1007/bf00211779](https://doi.org/10.1007/bf00211779))
- Lefevre, J., Dayie, K., Peng, J., and Wagner, G. (1996). Internal mobility in the partially folded DNA binding and dimerization domains of GAL4: NMR analysis of the N-H spectral density functions. *Biochemistry*, **35**(8), 2674–2686. ([10.1021/bi9526802](https://doi.org/10.1021/bi9526802))

Generic parts of relax

The following subsections will list the citations for the parts of relax independent of the specific analyses.

Model selection references

The citation for the model selection component of relax is:

- d'Auvergne, E. J. and Gooley, P. R. (2003). The use of model selection in the model-free analysis of protein dynamics. *J. Biomol. NMR*, **25**(1), 25–39. ([10.1023/a:1021902006114](https://doi.org/10.1023/a:1021902006114))

The base citations for the specific model selection techniques of AIC, AICc, and BIC are respectively:

- Akaike, H. (1973). Information theory and an extension of the maximum likelihood principle. In: Petrov, B. N. and Csaki, F. (eds.): *Proceedings of the Second International Symposium on Information Theory*. Budapest, pages 267–281, Akademia Kiado
- Hurvich, C. M. and Tsai, C. L. (1989). Regression and time-series model selection in small samples. *Biometrika*, **76**(2), 297–307. ([10.1093/biomet/76.2.297](https://doi.org/10.1093/biomet/76.2.297))
- Schwarz, G. (1978). Estimating dimension of a model. *Ann. Stat.*, **6**(2), 461–464. ([10.1214/aos/1176344136](https://doi.org/10.1214/aos/1176344136))

Other citations

If you believe that other citations should be included in this chapter, please contact the relax users mailing list (relax-users at gna.org).

Part I

The basics

Chapter 1

Introduction

The program relax is designed for the study of molecular dynamics through the analysis of experimental NMR data. Organic molecules, proteins, RNA, DNA, sugars, and other biomolecules are all supported. It was originally written for the model-free analysis of protein dynamics, though its scope has been significantly expanded. It is a community driven project created by NMR spectroscopists for NMR spectroscopists. It supports many analysis types including:

Model-free analysis - the Lipari and Szabo model-free analysis of NMR relaxation data

R₁ and R₂ - the exponential curve fitting for the calculation of the R_x NMR relaxation rates.

NOE - the calculation of the steady-state NOE NMR relaxation data.

Data consistency - the consistency testing of multiple field NMR relaxation data.

RSDM - Reduced Spectral Density Mapping.

Frame order and N-state model - study of domain motions via the N-state model and frame order dynamics theories using anisotropic NMR parameters such as RDCs and PCSs.

Stereochemistry - investigations of absolute stereochemistry of flexible molecules.

The aim of relax is to provide a seamless and extremely flexible environment able to accept input in any format produced by other NMR software, able to faultlessly create input files, control, and read output from various programs including Modelfree and Dasha, output results in many formats, and visualise the data by controlling programs such as Grace, OpenDX, MOLMOL, and PyMOL. All data analysis tools from optimisation to model selection to Monte Carlo simulations are inbuilt into relax. Therefore the use of additional programs is optional.

The flexibility of relax arises from the choice of relax's scripting capabilities, its Python prompt interface, or its graphical user interface (GUI). Extremely complex scripts can be created from simple building blocks to fully automate data analysis. A number of sample

scripts have been provided to help understand script construction. In addition, any of Python's powerful features or functions can be incorporated as the script is executed as an arbitrary Python source file within relax's environment. The modules of relax can also be used as a vast library of dynamics related functions by your own software.

relax is free software (free as in freedom) which is licenced under the GNU General Public Licence (GPL). You are free to copy, modify, or redistribute relax under the terms of the GPL.

1.1 Program features

1.1.1 Literature

The primary references for the program relax are [d'Auvergne and Gooley \(2008a\)](#) and [d'Auvergne and Gooley \(2008b\)](#). To properly cite the various parts of relax used in your analysis, please see Chapter [on page xxi](#).

1.1.2 Supported NMR theories

The following relaxation data analysis techniques are currently supported by relax:

- Model-free analysis ([Lipari and Szabo \(1982a,b\)](#); [Clore et al. \(1990\)](#) and the specific implementation of [d'Auvergne and Gooley \(2003, 2006, 2007, 2008a,b\)](#)). This includes the hybridisation of global diffusion models to study residual domain dynamics ([Horne et al., 2007](#)).
- Reduced spectral density mapping ([Farrow et al., 1995](#); [Lefevre et al., 1996](#)).
- Consistency testing – the validation of multiple field NMR relaxation data ([Morin and Gagné, 2009a](#); [Fushman et al., 1999](#)).
- Exponential curve fitting (to find the R_1 and R_2 relaxation rates).
- Steady-state NOE calculation.
- Determination of absolute stereochemistry of flexible molecules via the N-state model using isotropic and anisotropic NMR parameters such as NOE, ROE, and RDC combined with MD simulation or simulated annealing, and ORD ([Sun et al., 2011](#)).
- The N-state model for investigating domain motions.
- The frame order theory.
- Conformational analysis of paramagnetically tagged molecules via the N-state model ([Erdelyi et al., 2011](#)).
- Analysis and comparison of ensembles of structures using RDCs, PCSs, NOEs, etc. (the N-state model of dynamics).

The future

At some time in the future the following techniques are planned to be implemented within relax:

- Relaxation dispersion.
- All other dynamics analyses.

Because relax is free software, if you would like to contribute addition features, functions, or modules which you have written for your own publications for the benefit of the field, almost anything relating to molecular dynamics may be accepted. Please see the Open Source chapter on page 29 for more details.

1.1.3 Data analysis tools

The following tools are implemented as modular components to be used by any data analysis technique:

- Numerous high-precision optimisation algorithms.
- Model selection ([d'Auvergne and Gooley, 2003](#); [Chen et al., 2004](#)):
 - Akaike's Information Criteria (AIC).
 - Small sample size corrected AIC (AICc).
 - Bayesian or Schwarz Information Criteria (BIC).
 - Bootstrap model selection.
 - Single-item-out cross-validation (CV).
 - Hypothesis testing ANOVA model selection (only the model-free specific technique of [Mandel et al. \(1995\)](#) is supported).
- Monte Carlo simulations (error analysis for all data analysis techniques).
- Model elimination – the removal of failed models prior to model selection ([d'Auvergne and Gooley, 2006](#)).

1.1.4 Data visualisation

The results of an analysis, or any data input into relax, can be visualised using a number of programs:

MOLMOL 1D data can be mapped onto a structure either by the creation of MOLMOL macros or by direct control of the program.

PyMOL 3D objects such as the diffusion tensor representation can be displayed with the structure.

Grace any 2D data can be plotted.

OpenDX The chi-squared space of models with three parameters can be mapped and 3D images of the space produced.

1.1.5 Interfacing with other programs

relax can create the input files, execute in-line, and then read the output of the following programs. These programs can be used as optimisation engines replacing the minimisation algorithms built into relax:

- Dasha (model-free analysis).
- Modelfree (model-free analysis).

1.1.6 The user interfaces (UI)

relax can be used through the following UIs:

The prompt this is the primary interface of relax. Rather than reinventing a new command language, relax's interface is the powerful Python prompt. This gives the power user full access to a proven programming language. See Figure 1.1 for a screenshot.

Scripting this provides a more powerful and flexible framework for controlling the program. The script will be executed as Python code enabling advanced programming for automating data analysis. All the features available within the prompt environment are accessible to the script. See Figure 1.2 for a screenshot.

GUI the graphical user interface provides a sub-set of relax's features - the automatic R₁ and R₂ relaxation rate curve-fitting, the NOE calculations, and the automatic model-free analysis provided by the `dauvergne_protocol` module ([d'Auvergne and Gooley, 2008b](#)). See Figure 1.3 for a screenshot.

1.2 How to use relax

1.2.1 The prompt

The primary interface of relax is the prompt. After typing “`relax`” within a terminal you will be presented with

```
relax>
```

This is the Python prompt which has been tailored specifically for relax. You will hence have full access, if desired, to the power of the Python programming language to manipulate your data. You can for instance type

The screenshot shows a window titled "2.1.1 : python" containing the relax 2.1.1 molecular dynamics software. The window has a menu bar with File, Edit, View, Scrollback, Bookmarks, Settings, and Help. Below the menu is the relax 2.1.1 welcome message, which includes the copyright notice (Copyright (C) 2001-2006 Edward d'Auvergne, Copyright (C) 2006-2012 the relax development team), a license notice (GNU General Public License (GPL)), and instructions for using the help function. It also displays the processor fabric as a Uni-processor. The main area shows a command-line session:

```

relax> help
For assistance in using a function, simply type 'help(function)'. All functions can be viewed by
hitting the [TAB] key. In addition to functions, if 'help(object)' is typed, the help for the
python object is returned. This system is similar to the help function built into the python
interpreter, which has been renamed to help_python, with the interactive component removed. For the
interactive python help system, type 'help_python()'.

relax> pipe.create('test', 'mf')
relax> pipe.create('noe test', 'noe')
relax> pipe.display()
Data pipe name      Data pipe type      Bundle      Current
'test'              mf                  None        *
'noe test'          noe                 None        *

relax> minimise()

Over-fit spin deselection.

RelaxError: The sequence data does not exist.

relax> reset()
relax> state.load('results')■

```

Figure 1.1: A screenshot of relax being run in the primary prompt mode.

```
relax> print("Hello World")
```

the result being

```
relax> print("Hello World")
Hello World
relax>
```

Or using relax as a calculator

```
relax> (1.0 + (2 * 3))/10
0.6999999999999996
relax>
```

1.2.2 Python

relax has been designed such that knowledge about Python is not required to be able to fully use the program. A few basics though will aid in understanding relax.

A number of simple programming axioms includes that of strings, integers, floating point numbers, and lists. A string is text and within Python (as well as relax) this is delimited by either single or double quotes. An integer is a number with no decimal point whereas a float is a number with a decimal point. A list in Python (called an array in other languages) is a list of anything separated by commas and delimited by square brackets, an example is [0, 1, 2, 'a', 1.2143235].

```

File Edit View Bookmarks Settings Help
[edward@localhost 1.3.15]$ ./relax simple_script.py

      relax 1.3.15
      Molecular dynamics by NMR data analysis
      Copyright (C) 2001-2006 Edward d'Auvergne
      Copyright (C) 2006-2012 the relax development team

This is free software which you are welcome to modify and redistribute under the conditions of the
GNU General Public License (GPL). This program, including all modules, is licensed under the GPL
and comes with absolutely no warranty. For details type 'GPL' within the relax prompt.

Assistance in using the relax prompt and scripting interface can be accessed by typing 'help' within
the prompt.

Processor fabric: Uni-processor.

script = 'simple_script.py'
-----
pipe.create('Dy test', 'N-state')
align_tensor.init(tensor='Dysprosium', params=(1.0278e-03, -1.4860e-03, 8.4778e-04, 5.7108e-04, 3.6500e-04), param_types=1)
rdc.calc_q_factors()
align_tensor.delete()
align_tensor.display()
-----
relax> pipe.create(pipe_name='Dy test', pipe_type='N-state')
relax> align_tensor.init(tensor='Dysprosium', params=(0.0010278, -0.001486, 0.00084778, 0.00057108, 0.000365), scale=1.0, angle_units='deg',
', param_types=1, errors=False)
relax> rdc.calc_q_factors(spin_id=None)
RelaxWarning: No RDC data exists, Q factors cannot be calculated.

relax> align_tensor.delete(tensor=None)
Removing the 'Dysprosium' tensor.

relax> align_tensor.display(tensor=None)
RelaxError: No alignment tensor data exists.

[edward@localhost 1.3.15]$ 

```

Figure 1.2: A screenshot of relax being run in scripting mode.

Probably the most important detail is that functions in Python require brackets around their arguments. For example

```
relax> minimise()
```

will commence minimisation however

```
relax> minimise
```

will do nothing.

The arguments to a function are simply a comma separated list within the brackets of the function. For example to save the program's current state type

```
relax> state.save('save', force=True)
```

Two types of arguments exist in Python – standard arguments and keyword arguments. The majority of arguments you will encounter within relax are keyword arguments however you may, in rare cases, encounter a non-keyword argument. For these standard arguments just type the values in, although they must be in the correct order. Keyword arguments consist of two parts – the key and the value. For example the key may be `file` and the value you would like to supply is “`R1.out`”. Various methods exist for supplying this argument. Firstly you could simply type “`R1.out`” into the correct position in the argument list. Secondly you can type `file='R1.out'`. The power of this second option is that argument order is unimportant. Therefore if you would like to change the default value of the very last argument, you don't have to supply values for all other arguments. The only catch is that standard arguments must come before the keyword arguments.

1.2.3 User functions

For standard data analysis a large number of specially tailored functions called “user functions” have been implemented. These are accessible from the relax prompt by simply typing the name of the function. An example is `help()`. An alphabetical listing of all accessible user functions together with full descriptions is presented later in this manual.

A few special objects which are available within the prompt are not actually functions. These objects do not require brackets at their end for them to function. For example to exit relax type

```
relax> exit
```

Another special object is that of the function class. This object is simply a container which holds a number of user functions. You can access the user function within the class by typing the name of the class, then a dot “.”, followed by the name of the user function. An example is the user function for reading relaxation data out of a file and loading the data into relax. The function is called “`read`” and the class is called “`relax_data`”. To execute the function, type something like

```
relax> relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
    res_num_col=1, data_col=3, error_col=4)
```

On first usage the relax prompt can be quite daunting. Two features exist to increase the usability of the prompt – the help system and tab completion.

1.2.4 The help system

For assistance in using a function simply type

```
relax> help(function)
```

In addition to functions if

```
relax> help(object)
```

is typed the help for the python object is returned. This system is similar to the help function built into the python interpreter, which has been renamed to `help_python`, with the interactive component removed. For the standard interactive python help system type

```
relax> help_python()
```

1.2.5 Tab completion

Tab completion is implemented to prevent insanity as the function names can be quite long – a deliberate feature to improve usability. The behaviour of the tab completion is very similar to that of the bash prompt.

Not only is tab completion useful for preventing RSI but it can also be used for listing all available functions. To begin with if you hit the [TAB] key without typing any text all available functions will be listed (along with function classes and other python objects).

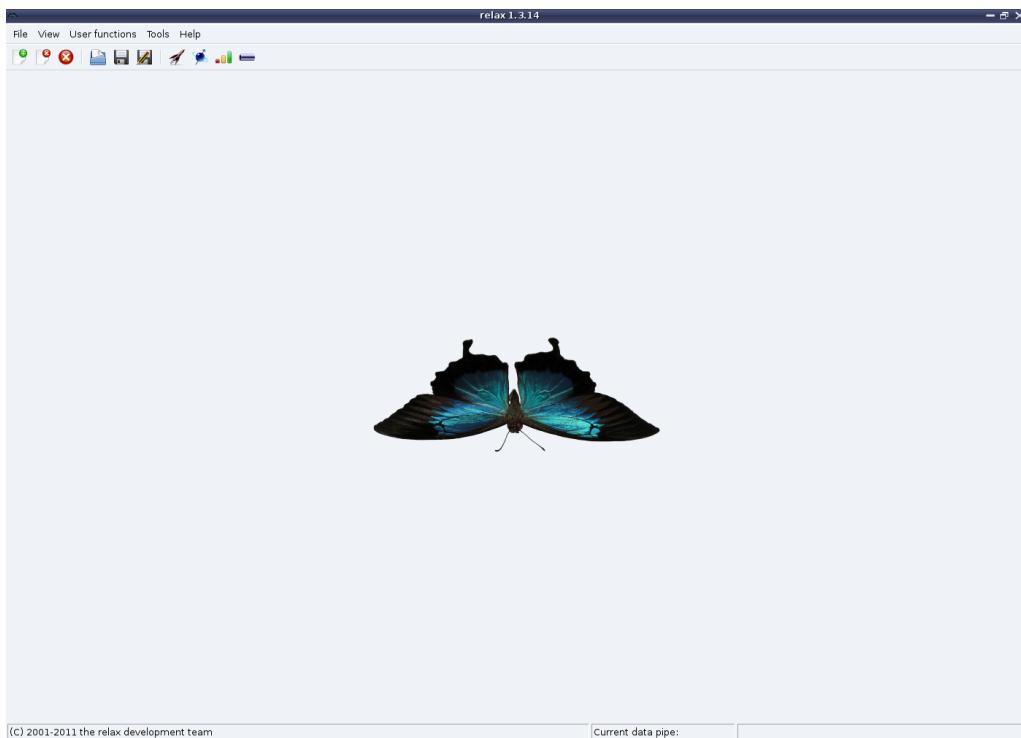


Figure 1.3: Screenshot of the relax GUI interface – the starting interface. To start one of the automated analyses, either the menu “File→New analysis” or the new analysis button in the toolbar should be selected.

This extends to the exploration of user functions within a function class. For example to list the user functions within the function class `model_free` type

```
relax> model_free.
```

The dot character at the end is essential. After hitting the [TAB] key you should see something like

```
relax| model_free.
model_free.__class__
model_free.__doc__
model_free.__init__
model_free.__module__
model_free.__relax__
model_free.__relax_help__
model_free.create_model
model_free.delete
model_free.remove_tm
model_free.select_model
relax> model_free.
```

All the objects beginning with an underscore are “hidden”, they contain information about the function class and should be ignored. From the listing the user functions `copy`, `create_model`, `delete`, `remove_tm`, and `select_model` contained within `model_free` are all visible.

1.2.6 The data pipe

Within relax all user functions operate on data stored within the current data pipe. This pipe stores data as input, processed, or output as user functions are called. There are different types of data pipe for different analyses, e.g. a reduced spectral density mapping pipe, a model-free pipe, an exponential curve-fitting pipe, etc. Multiple data pipes can be created within relax and various operations performed in sequence on these pipes. This is useful for operations such as model selection whereby the function `model_selection` can operate on a number of pipes corresponding to different models and then assign the results to a newly created pipe. When running relax you choose which pipe you are currently in by using the `pipe.switch` user function to jump between pipes.

The flow of data through relax can be thought of as travelling through these pipes. User functions exist to transfer data between these pipes and other functions combine data from multiple pipes into one or vice versa. The simplest invocation of relax would be the creation of a single data pipe and with the data being processed as it is passing through this pipe.

The primary method for creating a data pipe is through the user function `pipe.create`. For example

```
relax> pipe.create('m1', 'mf')
```

will create a model-free data pipe labelled “`m1`”. The following is a table of all the types which can be assigned to a data pipe.

Data pipe type	Description
“ <code>ct</code> ”	Consistency testing of relaxation data
“ <code>frame_order</code> ”	The Frame Order analyses of domain motions
“ <code>jw</code> ”	Reduced spectral density mapping
“ <code>hybrid</code> ”	A special hybridised data pipe
“ <code>mf</code> ”	Model-free data analysis
“ <code>N-state</code> ”	N-state model of domain motions
“ <code>noe</code> ”	Steady state NOE calculation
“ <code>relax_fit</code> ”	Relaxation curve-fitting

1.2.7 The spin and interatomic data containers

Any data which is not considered global for the molecule, such as diffusion tensors, alignment tensors, global minimisation statistics, etc., are stored within two special structures of the data pipes. Any NMR data or information which is specific to an isolated spin system is stored within special spin containers. This includes for example relaxation data, CSA information, nuclear isotope type, chemical element type, model-free parameters, reduced spectral density mapping values, spin specific minimisation statistics and PCS data. NMR data or information which is defined as being between two spin systems, such as the magnetic dipole-dipole interaction involved in both NMR relaxation and RDC data, interatomic vectors and NOESY data, is stored within the interatomic data containers. The spin and interatomic data containers and their associated data can be manipulated using a multitude of the relax user functions.

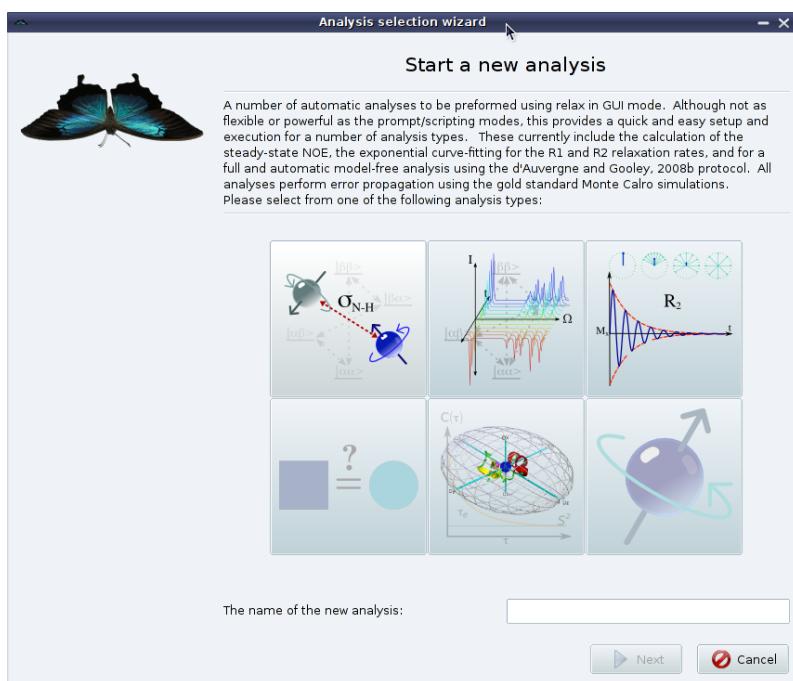


Figure 1.4: Screenshot of the relax GUI interface – the analysis selection wizard. From here, the steady-state NOE analysis, the R_1 and R_2 relaxation rates via exponential curve-fitting, and the automated model-free analysis can be selected.

1.2.8 Scripting

What ever is done within the prompt is also accessible through scripting (Figure 1.2). First type your commands into a text file ending in `*.py`. To use this mode of relax, you will need to open up a terminal in your respective operating system:

GNU/Linux: Here you have an incredible number of choices. If you don't have a preferred shell already, you could try one of `Konsole`, `GNOME Terminal` or even `XTerm` if you are a masochist.

Mac OS X: This is as simple as in GNU/Linux – just launch `Terminal.app` from the `Utilities` folder.

MS Windows: If your system supports it, you should install and use `Windows PowerShell`. The alternative is the nasty `cmd` command line terminal program which comes installed by default on all Windows versions. The `PowerShell`, although no where near as powerful as the Linux and Mac terminals, is a huge improvement on the ancient `cmd` program and will make relax much better to use on MS Windows.

Once your terminal is running, go to the directory containing your script using the `cd` command (if you do not know what this is, please see the documentation for your terminal program to understand some of its basic usage). Once you are in the correct directory, within the terminal type:

```
$ relax your_script.py
```

You will need to replace `your_script.py` with the name of your script. In most cases you would probably like to keep a log of all of the messages, warnings and errors relax produces for future reference. To active logging within relax, type:

```
$ relax --log log your_script.py
```

This will place all output (both STDOUT and STDERR) into the `log` file (you can choose any name for this log file). Alternatively you can both log the output and simultaneously see the messages in your terminal by typing:

```
$ relax --tee log your_script.py
```

These command line arguments could be replaced by IO redirection if this is a familiar concept to you, but note that these arguments are active also in the GUI mode whereby IO redirection in the terminal will have no effect. An example of a simple script which will minimise the model-free model “m4” after loading six relaxation data sets is

```

1 # Create the data pipe.
2 name = 'm4'
3 pipe.create(name, 'mf')
4
5 # Load the PDB file.
6 structure.read_pdb('1f3y.pdb')
7
8 # Set up the 15N and 1H spins.
9 structure.load_spins('@N', ave_pos=True)
10 structure.load_spins('@H', ave_pos=True)
11 spin.isotope('15N', spin_id='@N')
12 spin.isotope('1H', spin_id='@H')
13
14 # Load the relaxation data.
15 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
16     res_num_col=1, data_col=3, error_col=4)
16 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
17     res_num_col=1, data_col=3, error_col=4)
17 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
18     res_num_col=1, data_col=3, error_col=4)
18 relax_data.read(ri_id='R1_500', ri_type='R1', frq=500.0*1e6, file='r1.500.out',
19     res_num_col=1, data_col=3, error_col=4)
19 relax_data.read(ri_id='R2_500', ri_type='R2', frq=500.0*1e6, file='r2.500.out',
20     res_num_col=1, data_col=3, error_col=4)
20 relax_data.read(ri_id='NOE_500', ri_type='NOE', frq=500.0*1e6, file='noe.500.out',
21     res_num_col=1, data_col=3, error_col=4)
21
22 # Initialise the diffusion tensor.
23 diffusion_tensor.init((2e-8, 1.3, 60, 290), param_types=1, axial_type='prolate', fixed=
24     True)
24
25 # Create all attached protons.
26 sequence.attach_protons()
27
28 # Define the magnetic dipole-dipole relaxation interaction.
29 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
30 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)
31 interatom.unit_vectors()
32
33 # Define the CSA relaxation interaction.
34 value.set(-172 * 1e-6, 'csa')
35
36 # Select a preset model-free model.
```

```

37 model_free.select_model(model=name)
38
39 # Grid search.
40 grid_search(inc=11)
41
42 # Minimise.
43 minimise('newton')
44
45 # Finish.
46 results.write(file='results', force=True)
47 state.save('save', force=True)

```

Scripting is much more powerful than the prompt as advanced Python programming can be employed (see the file `relax_curve_diff.py` in the `sample_scripts` directory for an example).

Sample scripts

A few sample scripts have been provided in the directory `sample_scripts`. These can be copied and modified for different types of data analysis.

1.2.9 The test suite

To test that the program functions correctly, relax possesses an inbuilt test suite. The suite is a collection of simple tests which execute or probe different parts of the program checking that the software runs without problem. The test suite is executed by running relax using the command

```
$ relax --test-suite
```

Alternatively the three components of the test suite – system tests, unit tests, and GUI tests – can be run separately with

```

$ relax --system-tests
$ relax --unit-tests
$ relax --gui-tests

```

1.2.10 The GUI

If the wxPython module is installed on your system, you will have access to the GUI interface of relax. To launch relax in GUI mode, type either

```
$ relax -g
```

or

```
$ relax --gui
```

In most cases you will probably like to have a permanent copy of all the messages, warnings, and errors relax produces for future reference. In such a case you could run the GUI with:

```
$ relax --gui --log log
```

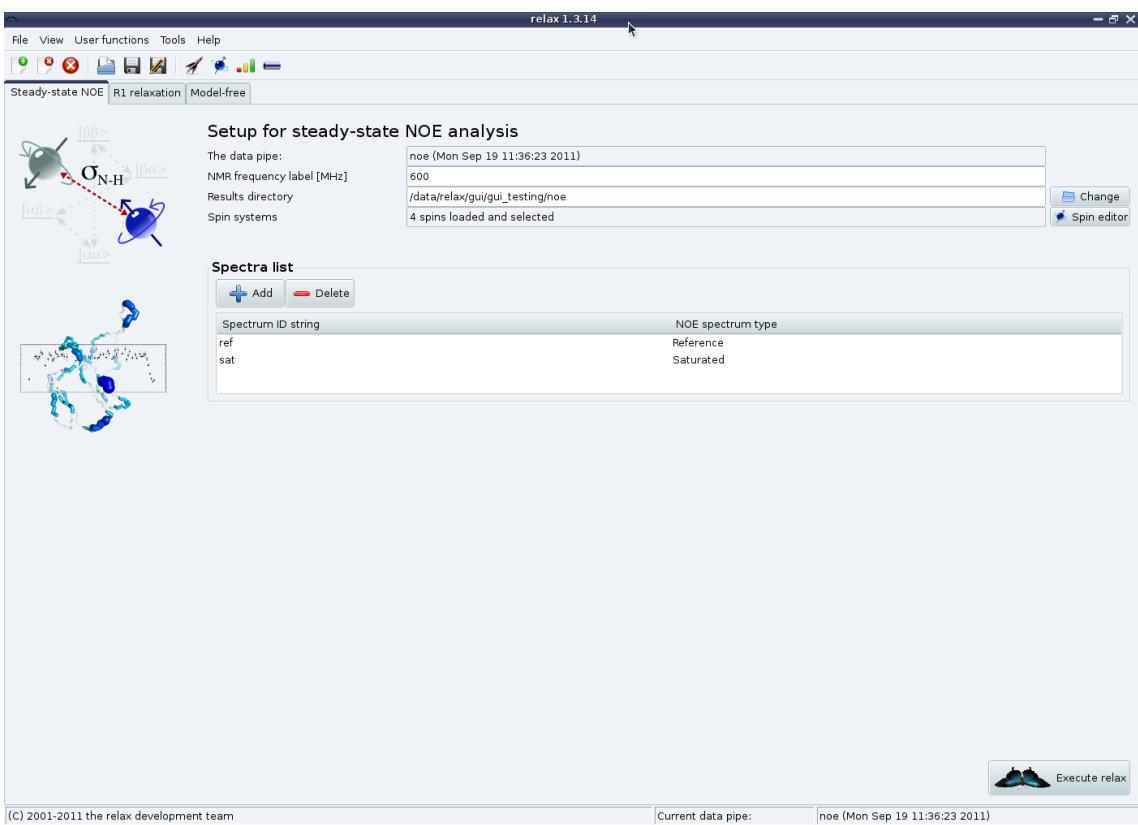


Figure 1.5: Screenshot of the relax GUI interface – the steady-state NOE analysis.

This will place all of the output into the `log` file.

The GUI is currently an interface to the automated analyses, providing an easy way to perform quick analyses. The interface consists of a tab for each analysis. By clicking on the “File→New analysis” menu entry or the “New analysis” toolbar button, the analysis wizard will appear (see Figure 1.4). The following analyses can be set up using this wizard:

Steady-state NOE: this provides access to the steady-state NOE calculation with pseudo Monte Carlo simulations for error analysis (this falls back to bootstrapping as this is a calculation rather than optimisation). See Figure 1.5 on page 15.

R₁ and R₂ : these provide easy access to optimisations and error analysis for the R₁ and R₂ relaxation rates via exponential curve-fitting (see Figures 1.6 and 1.7 on pages 16 and 17).

Model-free analysis : A fully automatic model-free protocol is provided in another tab. This operates via the `dauvergne_protocol` module which implements the protocol of d’Auvergne and Gooley (2008b) (see Figure 1.8 on page 18).

A number of windows in the GUI provide user feedback or allow for the viewing and editing of data. These include:

The relax controller : This window shows the progress of relax’s execution and displays

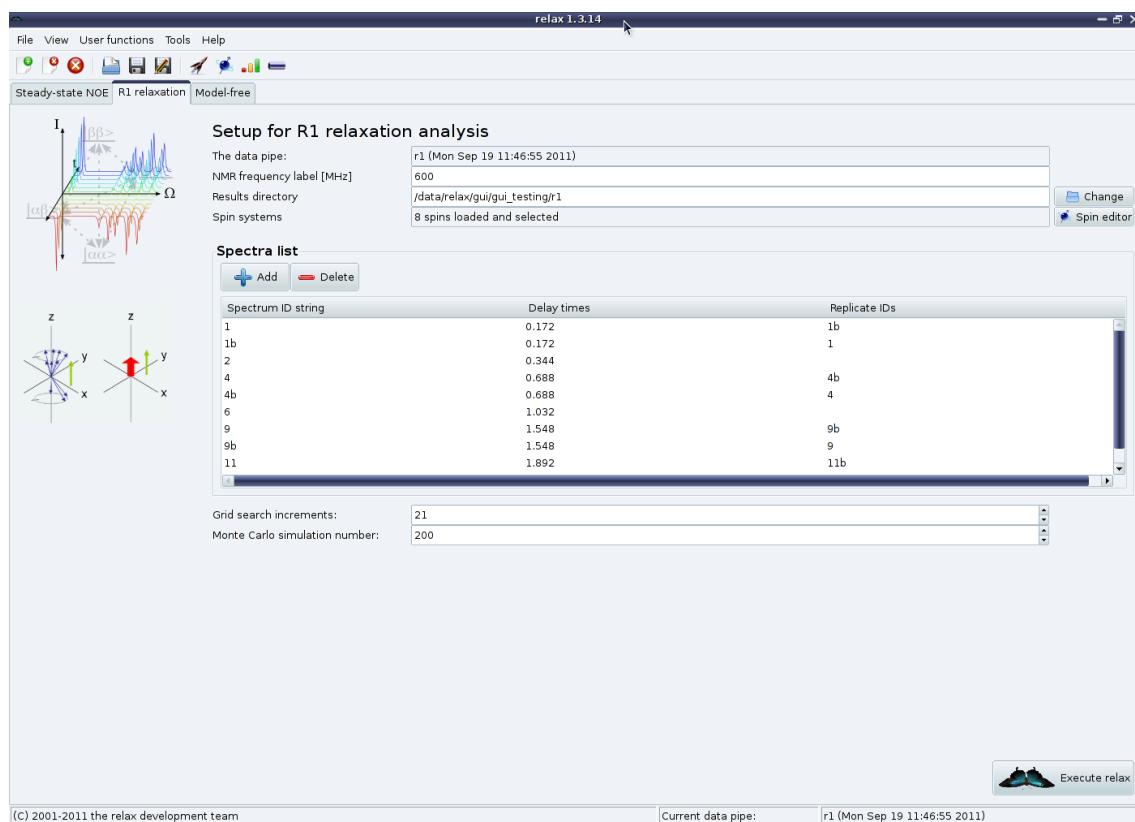


Figure 1.6: Screenshot of the relax GUI interface – the R_1 analysis.

relax's text output for checking if the analysis has been performed correctly and has completed successfully (see Figure 1.9).

Spin viewer window : This is used to load spins system information into the relax data store and to see the contents of the spin containers (see Figure 1.10).

Results viewer window : This presents a list of the results files which can be opened by double clicking for visualisation using a text editor, Grace, PyMOL, MOLMOL, etc (see Figure 1.11).

Data pipe editor : This window allows for easy manipulation of the data pipes of the relax data store (see Figure 1.12).

The relax prompt : This window gives access to the relax prompt (see Figure 1.13).

1.2.11 Access to the internals of relax

To enable advanced Python scripting and control, many parts of relax have been designed in an object oriented fashion. If you would like to play with internals of the program the entirety of relax is accessible by importation. For example all data is contained within the object called the relax data store which, to be able to access it, needs be imported by typing:

```
relax> from data_store import Relax_data_store; ds = Relax_data_store()
```

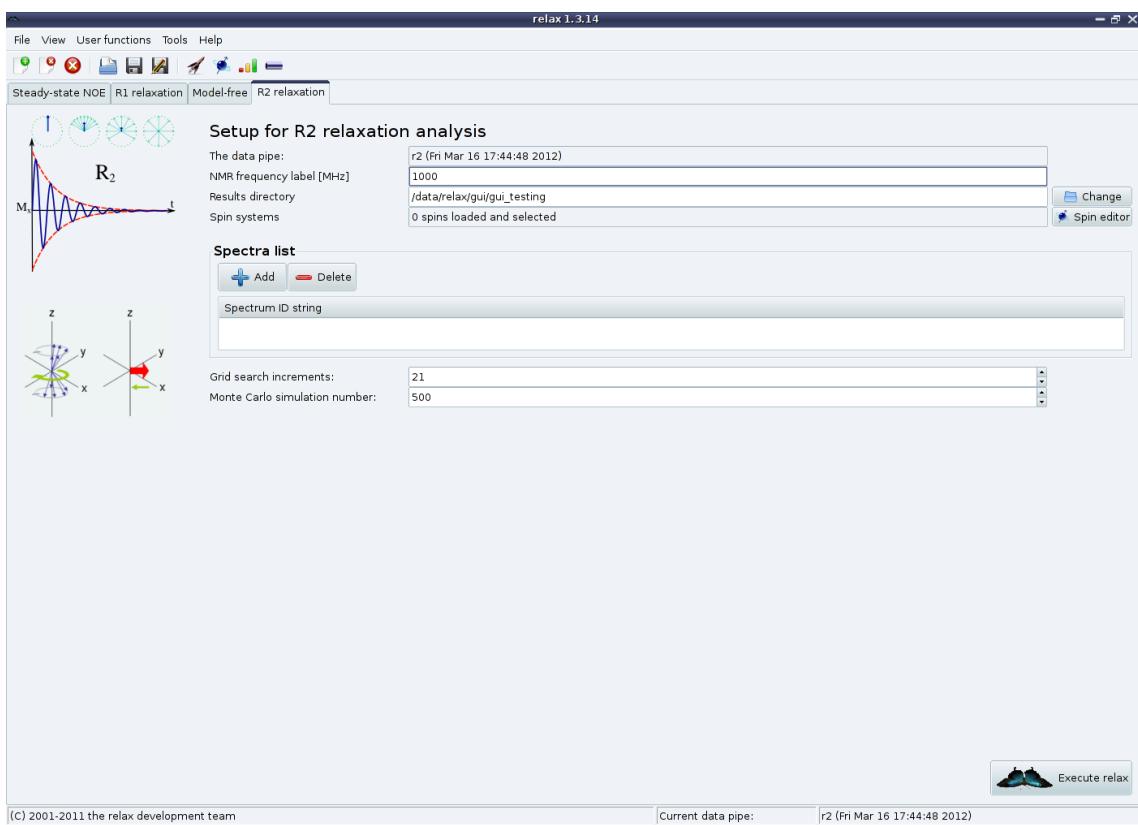


Figure 1.7: Screenshot of the relax GUI interface – the R_2 analysis.

The `ds` object is a dictionary type which contains the multiple data pipes. All of relax's packages, modules, functions, and classes are also accessible by import statements. For example to create a rotation matrix from three Euler angles in the z-y-z notation, type:

```
relax> alpha = 0.1342
relax> beta = 1.0134
relax> gamma = 2.4747
relax> from lib.geometry.rotations import euler_to_R_zyz
relax> from numpy import float64, zeros
relax> R = zeros((3,3), float64)
relax> euler_to_R_zyz(alpha, beta, gamma, R)
relax> print(R)
[[ -0.494666415429033 -0.557373756841289 -0.666813041737502]
 [ 0.219125193028791 -0.822460914570202  0.524921131013452]
 [-0.84100492699311   0.113545317776532  0.528978424497956]]
relax>
```

1.3 The multi-processor framework

1.3.1 Introduction to the multi-processor

Thanks to Gary Thompson's multi-processor framework, relax can be run on multi-core/multi-CPU systems or on clusters to speed up calculations. As most analyses are

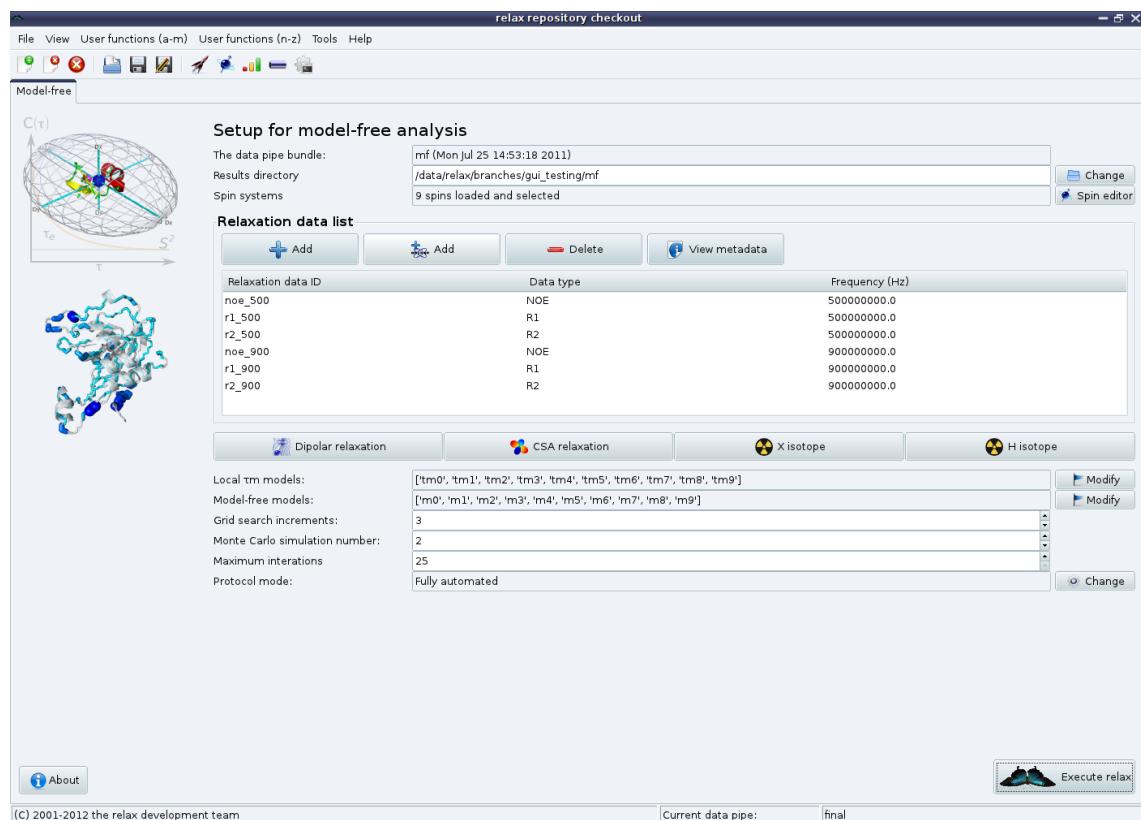


Figure 1.8: Screenshot of the relax GUI interface – the automated model-free analysis. The analysis is fully automated via a new model-free protocol as described in detail in Chapter 7. Clicking on the “About” button in the bottom left hand corner will give a full description of the protocol. For using this interface or any of the modern-day model-free protocols, data from at least two magnetic field strengths must be without question collected.

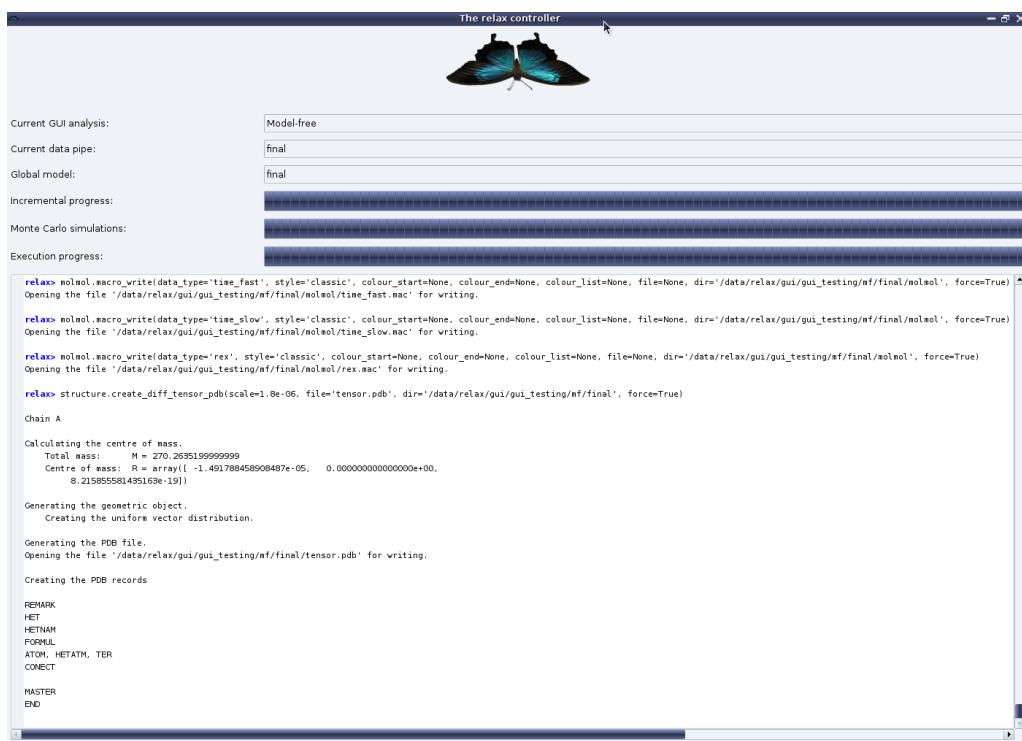


Figure 1.9: Screenshot of the relax GUI interface – the relax controller window. The purpose of the controller is for feedback. It shows the current analysis and current data pipe, a number of progress gauges, and the relax text output.

relatively quick and would not benefit from the multi-processor framework, only the model-free and frame order analyses have currently been parallelised to run within this framework. To use the multi-processor framework, the following should be installed:

OpenMPI: This is the most commonly used Message Passing Interface (MPI) protocol software. The rest of this manual will assume that this is the implementation in use. If another implementation is used, please see the specific documentation for that software for how to set up a program to run via MPI.

mpi4py: This dependency is essential for running in MPI mode in relax. If you would like to use another Python implementation to access the MPI protocol, please consider becoming a relax developer.

1.3.2 Usage of the multi-processor

If you have access to a 256 node cluster and can run calculations on all nodes, assuming that the `dauvergne_protocol.py` automated model-free analysis sample script will be used (after modification for the system under study), relax can be executed by typing:

```
$ mpirun -np 257 /usr/local/bin/relax --multi='mpi4py' --tee log dauvergne_protocol.py
```

Note that the argument `-np` value is one more than the number of slaves you would like to run. You should then see the following text in the initial relax printout:

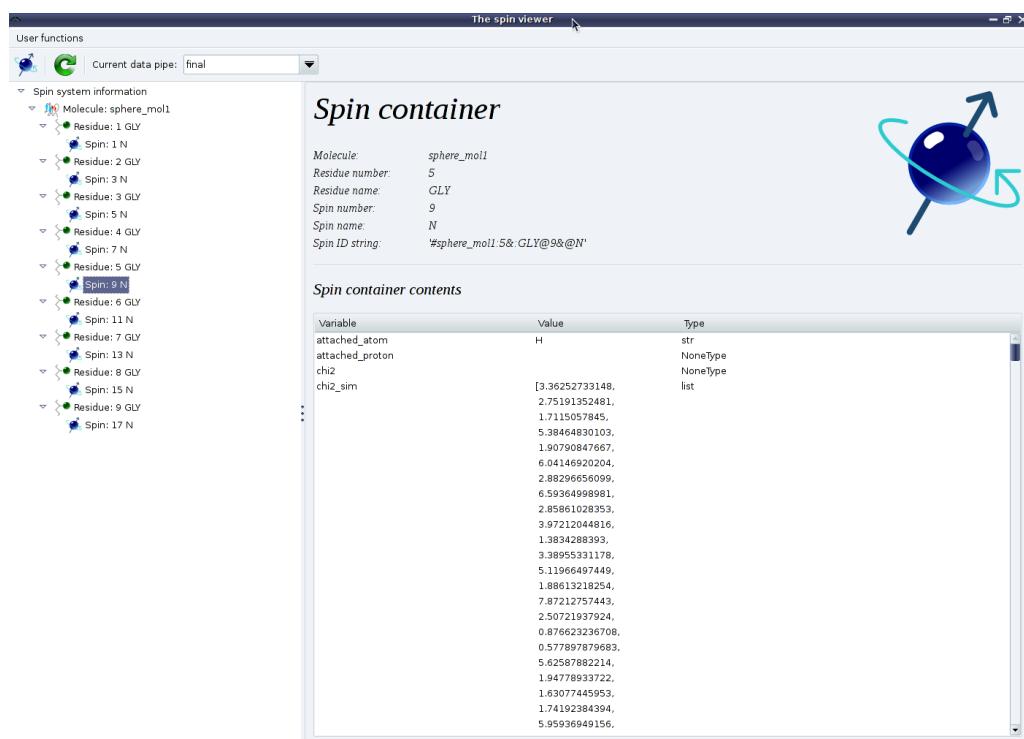


Figure 1.10: Screenshot of the relax GUI interface – the spin viewer window. This viewer is designed for easy addition and manipulation of spin systems within the relax data store. The window is accessible via the “View→Spin viewer” menu entry, typing “[Ctrl-T]”, the spin viewer button in the toolbar, or the “spin editor” button within the auto-analysis tabs.

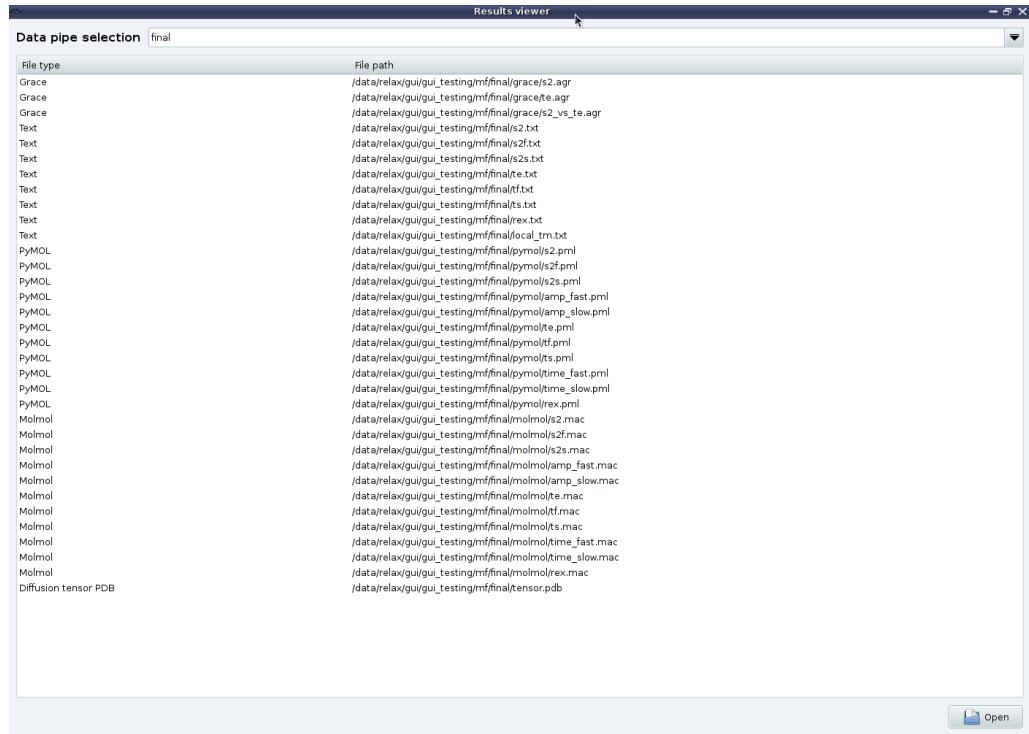


Figure 1.11: Screenshot of the relax GUI interface – the results viewer window. At the end of one of the automated analyses, a number of results files will be created. This can include text files containing the results, 2D Grace plots of the results, PyMOL and MOLMOL macros plotting the results onto the structure, diffusion tensor objects for viewing in PyMOL, etc. This window allows for easy opening of these results files.

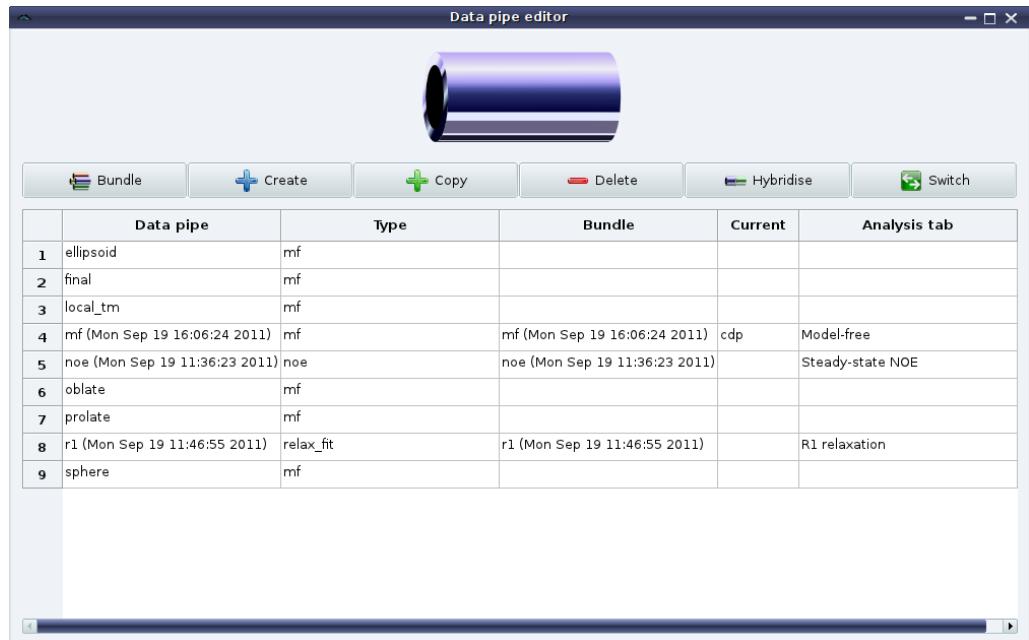


Figure 1.12: Screenshot of the relax GUI interface – the pipe editor window. One analysis may consist of one or more data pipes. And each analysis has its own unique set of data pipes. This editor allows for the easy manipulation of data pipes for advanced users.

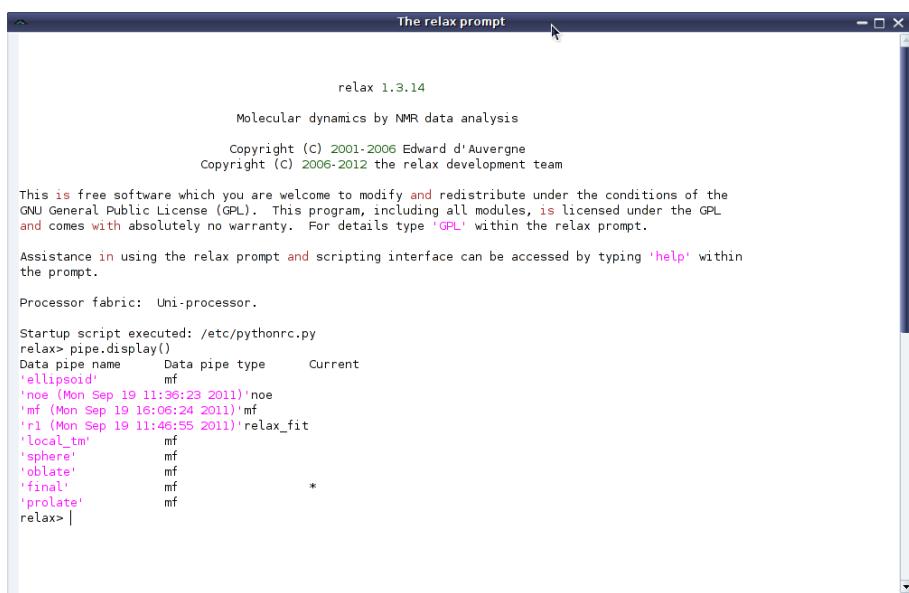


Figure 1.13: Screenshot of the relax GUI interface – the prompt window. This window mimics relax in the prompt user interface mode, and provides the full power of the prompt/script UI modes within the GUI.

Processor fabric: MPI 2.1 running via mpi4py with 256 slave processors & 1 master. Using Open MPI 1.4.3.

1.3.3 Further details

For a full description of the multi-processor framework and how to use it, please see Gary Thompson's official announcement on the [relax-devel mailing list](#).

1.4 Usage of the name relax

The program relax is so relaxed that the first letter should always be in lower case!

Chapter 2

Installation instructions

2.1 Dependencies

The following packages need to be installed before using relax:

Python: Version 2.5 or higher.

NumPy: Version 1.0.4 or higher. This package is used for most of the numerical calculations within relax.

SciPy: Version 0.7.1 or higher. This package is optional. It is required only for the frame order theory analyses.

wxPython: Version 2.8 or higher. This package is also optional. It is required for the operation of the graphical user interface (GUI).

mpi4py: Version 1.2 or higher. This optional dependency is essential for running relax in MPI multi-processor mode.

Older versions of these packages may work, use them at your own risk. If, for older dependency versions, errors do occur please submit a bug report to the bug tracker at <https://gna.org/bugs/?group=relax>. That way a solution may be created for the next relax release.

Note that only the official Python distribution from <http://python.org> is supported. If you use the Enthought Python Distribution (EPD) or other non-official distributions you may encounter problems with the relax C modules, the graphical user interface, or other issues. These alternative distributions are to be used at your own risk. Any issues encountered will not be considered as relax bugs.

2.2 Installation

2.2.1 The source releases

Two types of software packages are available for download – the precompiled and source distribution. Currently only relaxation curve-fitting requires compilation to function and all other features of relax will be fully functional without compilation. If relaxation curve-fitting is required but no precompiled version of relax exists for your operating system or architecture then, if a C compiler is present, the C code can be compiled into the shared objects files `*.so`, `*.pyd` or `*.dylib` which are loaded as modules into relax. To build these modules the Scons system from <http://scons.org/> is required. This software requires the Python and numpy header files installed. Once Scons is installed type

```
$ scons
```

in the base directory where relax has been installed and the C modules should, hopefully, compile without any problems. Otherwise please submit a bug report to the bug tracker at <https://gna.org/bugs/?group=relax>.

2.2.2 Installation on GNU/Linux

To install the program relax on a GNU/Linux system download either the precompiled distribution labelled `relax-x.x.x.GNU-Linux.arch.tar.bz2` matching your machine architecture or the source distribution `relax-x.x.x.src.tar.bz2`. A number of installation methods are possible. The simplest way is to switch to the user “root”, unpack and decompress the archive within the `/usr/local` directory by typing, for instance

```
$ tar jxvf relax-x.x.x.GNU-Linux.i686.tar.bz2
```

then create a symbolic link in `/usr/local/bin` by moving to that directory and typing

```
$ ln -s .../relax/relax .
```

and finally possibly creating the byte-compiled Python `*.pyc` files to speed up the start time of relax by typing

```
$ python -m compileall .
```

in the relax base directory. Alternatively if the Scons system is installed, by typing as the root user

```
$ scons install
```

in the relax base directory, a directory in `/usr/local/` called `relax` will be created, all the uncompressed and untarred files will be copied into this directory, a symbolic link in `/usr/local/bin` to the file `/usr/local/relax/relax` will be created, and then finally the Python `*.pyc` files will be byte-compiled. To change the installation path to a non-standard location the Scons script `sconstruct` in the base relax directory should be modified by changing the variable `INSTALL_PATH` to point to the desired location.

2.2.3 Installation on MS Windows

In addition to the above dependencies, running relax on MS Windows requires a number of additional programs. These include:

pyreadline: Version 1.3 or higher.

ctypes: The pyreadline package requires ctypes.

To install, simply download the pre-compiled binary distribution `relax-x.x.x.Win32.zip` or the source distribution `relax-x.x.x.src.zip` and extract the files to `C:\Program Files\relax-x.x.x`. Then add this directory to the system environment path (in Windows XP, right click on “My Computer”, go to “Properties”, click on the “Advanced” tab, and click on the “Environment Variables” button. Then double click on the “Path” system variable and add the text “`;C:\Program Files\relax-x.x.x`” to the end of variable value field. The Python installation must also be located on the path (add the text “`;C:\Python27`”, changing the text to point to the correct directory, to the field). To run the program from any directory inside the Windows command prompt (or dos prompt) type:

```
C:\> relax
```

Note that the pre-compiled binary distribution was built using a specific Python version and that that version may need to be installed for the modules to be loaded. More details are given on the [download](#) webpage.

2.2.4 Installation on Mac OS X

There are three ways of installing relax on a Mac. These are described at <http://www.nmr-relax.com/download.html> and are the pre-compiled relax application, the Fink or the source releases.

The relax application

The stand-alone relax application requires none of the dependencies listed above to be installed. It is a universal binary compiled for the i386, x86-64 and PPC CPU architectures (fat3) using the Mac OS X 10.5 framework. It should therefore run on Leopard, Snow Leopard, and Lion. This very large bundle does not require system administrator access to run.

Fink

Certain relax versions are available for Mac OS X within the Fink project. These can be installed for Python 2.7 with the command:

```
> fink install relax-py27
```

The relax releases packaged within Fink can be browsed at <http://pdb.finkproject.org/pdb/browse.php?name=relax>. If the desired version is

not available, please download the relevant source package below or contact the fink project using the “Maintainer” email address given in the relax fink pages.

Note that when installing via fink, all the dependencies will be automatically selected and installed as well. Although automatic, when starting from scratch that there could be well over 250 source packages that need to be compiled (to set up the full GNU compilation chain and other libraries which are then required to build Python, numpy, scipy, etc.). This may take anywhere between 2 days to over a week (don’t forget to mention this fact to your poor sys-admin).

The fink relax packages for different Python versions are [relax-py27](#), [relax-py26](#), [relax-py25](#) and [relax-py24](#).

Source release

See Section [2.2.1](#) on page [24](#).

2.2.5 Installation on your OS

For all others systems, please use the source distribution files and the Scons software to build the C modules.

2.2.6 Running a non-compiled version

Compilation of the C code is not essential for running relax, however certain features of the program will be disabled. Currently only the exponential curve-fitting for determining the R₁ and R₂ relaxation rates requires compilation. To run relax without compilation install the dependencies detailed above, download the source distribution which should be named `relax-x.x.x.src.tar.bz2`, extract the files, and then run the file called `relax` in the base directory.

2.3 Optional programs

The following is a list of programs which can be used by relax although they are not essential for normal use.

2.3.1 Grace

Grace is a program for plotting two dimensional data sets in a professional looking manner. It is used to visualise parameter values. It can be downloaded from <http://plasma-gate.weizmann.ac.il/Grace/>.

2.3.2 OpenDX

Version 4.1.3 or compatible. OpenDX is used for viewing the output of the space mapping function and is executed by passing the command `dx` to the command line with various options. The program is designed for visualising multidimensional data and can be found at <http://www.opendx.org/>.

2.3.3 Molmol

Molmol is used for viewing the PDB structures loaded into the program and to display parameter values mapped onto the structure.

2.3.4 PyMOL

PDB structures can also be viewed using PyMOL. This program can also be used to display geometric objects generated by relax for representing physical concepts such as the diffusion tensor and certain cone diffusion models.

2.3.5 Dasha

Dasha is a program used for model-free analysis of NMR relaxation data. It can be used as an optimisation engine to replace the minimisation algorithms implemented within relax.

2.3.6 Modelfree4

Art Palmer's Modelfree4 program is also designed for model-free analysis and can be used as an optimisation engine to replace relax's high precision minimisation algorithms.

Chapter 3

Open source infrastructure

3.1 The relax web sites

The main web site for relax is <http://www.nmr-relax.com>. From these pages general information about the program, links to the latest documentation, links to the most current software releases, and information about the mailing lists are available. There are also Google search capabilities built into the pages for searching both the HTML version of the manual and the archives of the mailing lists.

The relax web site is hosted by the Gna! project (<https://gna.org/>) which is described as “a central point for development, distribution and maintenance of Libre Software (Free Software) projects”. relax is a registered Gna! project and its primary Gna! web site is <https://gna.org/projects/relax>. This site contains many more technical details than the main web site.

3.2 The mailing lists

A number of mailing lists have been created covering different aspects of relax. These include the announcement list, the relax users list, the relax development list, and the relax committers list.

3.2.1 relax-announce

The relax announcement list “relax-announce at gna.org” is reserved for important announcements about the program including the release of new program versions. The amount of traffic on this list is relatively low. If you would like to receive information about relax you can subscribe to the list by visiting the information page at <https://mail.gna.org/listinfo/relax-announce/>. Previous announcements can be viewed at <https://mail.gna.org/public/relax-announce/>.

3.2.2 relax-users

If you would like to ask questions about relax, discuss certain features, receive help, or to communicate on any other subject related to relax the mailing list “relax-users at gna.org” is the place to post your message. To subscribe to the list go to the relax-users information page at <https://mail.gna.org/listinfo/relax-users/>. You can also browse the mailing list archives at <https://mail.gna.org/public/relax-users/>.

3.2.3 relax-devel

A second mailing list exists for posts relating to the development of relax. The list is “relax-devel at gna.org” and to subscribe go to the relax-devel information page at <https://mail.gna.org/listinfo/relax-devel/>. Feature requests, program design, or any other posts relating to relax’s structure or code should be sent to this list instead. The mailing list archives can be browsed at <https://mail.gna.org/public/relax-devel/>.

3.2.4 relax-commits

One last mailing list is the relax commits list. This list is reserved for automatically generated posts created by the version control software which looks after the relax source code and these web pages. If you would like to become a developer you can subscribe to the list at relax-commits information page <https://mail.gna.org/listinfo/relax-commits/>. The list can also be browsed at <https://mail.gna.org/public/relax-commits/>.

3.2.5 Replying to a message

When replying to a message on these lists remember to hit ‘respond to all’ so that the mailing list is included in the CC field. Otherwise your message will only be sent to the original poster and not return back to the list. Only messages to relax-users and relax-devel will be accepted. If you are using Gmail’s web based interface, please do not click on ‘Edit Subject’ as this currently mangles the email headers, creates a new thread on the mailing list, and makes it difficult to follow the thread.

3.3 Reporting bugs

One of the philosophies in the construction of relax is that if there is something which is not immediately obvious then that is considered a design bug. If any flaws in relax are uncovered including general design flaws, bugs in the code, or documentation issues these can be reported within relax’s bug tracker system. The link to submit a bug is <https://gna.org/bugs/?group=relax&func=additem> while the main page for browsing, submitting, viewing the statistics, or searching through the database is at <https://gna.org/bugs/?group=relax>. Please do not report bugs to personal email addresses or to the mailing lists.

When reporting a bug please include as much information as possible so that the problem can be reproduced. Include information such as the release version or the revision number if the repository sources are being used. Also include all the steps performed in order to trigger the bug. Attachment of files is allowed so scripts and subsets of the input data can be included. However please do not attach large files to the report. Prior to reporting the bug try to make sure that the problem is indeed a bug and if you have any doubts please feel free to ask on the relax-users mailing list. To avoid duplicates be sure that the bug has not already been submitted to the bug tracker. You can search the bugs from the page <https://gna.org/project/search.php?group=relax>.

Once the bug has been confirmed by one of the relax developers you may speed up the resolution of the problem by trying to fix the bug yourself. If you do wish to play with the source code and try to fix the issue see the relax development chapter of this manual on how to check out the latest sources (Chapter 10 on page 141), how to generate a patch (which is just the output of diff in the ‘unified’ format), and the guidelines for the format of the code.

3.4 Latest sources – the relax repositories

relax’s source code is kept within a version control system called Subversion (<http://subversion.tigris.org/>). Subversion or SVN allows fine control over the development of the program. The repository contains all information about every change ever made to the program. To learn more about the system the Subversion book located at <http://svnbook.red-bean.com/> is a good place to start. The contents of the relax repository can be viewed on-line at <http://svn.gna.org/viewcvs/relax/>. The current sources can be downloaded using the SVN protocol by typing

```
$ svn co svn://svn.gna.org/svn/relax/trunk relax-trunk
```

however if this does not work, try the command

```
$ svn co http://svn.gna.org/svn/relax/trunk relax-trunk
```

to download using the HTTP protocol. The entire relax repository is backed up daily to <http://svn.gna.org/daily/relax.dump.gz>.

3.5 News

Summaries of the latest news on relax can be found on the relax web site <https://gna.org/projects/relax>. However more information can be found at the dedicated news page <https://gna.org/news/?group=relax>.

3.6 The relax distribution archives

The relax distribution archives, the files to download to install relax, can be found at <http://download.gna.org/relax/>. If a compiled binary distribution for your architecture

does not exist you are welcome to create this distribution yourself and submit it for inclusion in the relax project. To do this a number of steps are required. Firstly, the code to each relax release or version resides in the ‘tags’ directory of the relax repository. To check out version 2.1.1 for example type

```
$ svn co svn://svn.gna.org/svn/relax/tags/2.1.1 relax
```

Again the sources are available through HTTP by typing

```
$ svn co http://svn.gna.org/svn/relax/tags/2.1.1 relax
```

The binary distribution can then be created for your architecture by shifting to the main directory of the checked out sources and typing

```
$ cd relax  
$ scons binary_dist
```

At the end SCons will attempt to make a GPG signature for the newly created archive. However this will fail as the current relax private GPG key is not available for security reasons. If the SCons command fails, excluding the GPG signing, please submit a bug report with as much information possible including the details described next to <https://gna.org/bugs/?group=relax&func=additem> (the python and SCons version numbers may also be useful). Once the file has been created post a message to the relax development mailing list describing the compilation and the creation of the archive, the relax version number, the machine architecture, operating system, and the name of the new file. Do not attach the file though. You will then receive a response explaining where to send the file to. For security the archive will be thoroughly checked and if the source code is identical to that in the repository and the C modules are okay, the file will be GPG signed and uploaded to <http://download.gna.org/relax/>.

Chapter 4

The relax data model

4.1 The concept of the relax data model

To begin to understand how to use relax, a basic comprehension of the relax data model is needed. The data model includes the concepts of the relax data store, the data pipes, the molecule, residue and spin data structures and the interatomic data containers. These concepts are independent of the specific analyses presented in the next chapters and are important for setting up relax.

4.2 The data model

4.2.1 The relax data store

All permanent data handled by relax is kept in a structure known as the relax data store. This structure is initialised when relax is launched. The data store is primarily organised into a series of objects known as data pipes, and all usage of relax revolves around the flow of information in these data pipes.

Data pipes



The first thing one must do when relax is launched is to create a data pipe. When using the GUI, a base data pipe will be created when opening one of the automatic analyses via the analysis selection window (see figure 1.4 on page 12). This will also create a data pipe bundle for the analysis (*vide infra*). Alternatively the data pipe editor window can be

used to create data pipes (see figure 1.12 on page 21). For the prompt/scripting modes, or the “User functions→pipe→create” menu entry, a data pipe can be initialised by specifying the unique name of the data pipe and the data pipe type:

```
1 pipe.create(pipe_name='NOE 1200 MHz', pipe_type='noe')
```

A number of relax operations will also create data pipes by merging a group of pipes or branching pre-existing pipes. See section 1.2.6 on page 11 for additional details.

All data not associated with spin systems will be stored in the base data pipe. This includes information such as global optimisation statistics, diffusion tensors, alignment tensors, 3D structural data, the molecule, residue and spin container data structure and the interatomic data containers. One data pipe from the set will be defined as being the current data pipe, and all operations in relax will effect data from this pipe. The `pipe.switch` user function in all UI modes can be used to change which pipe is the current data pipe. In the GUI, switching between analysis tabs will automatically switch the current data pipe to match the analysis being displayed.

Data pipe bundles



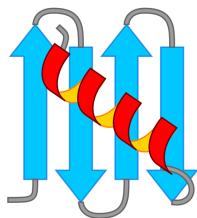
Related data pipes can be grouped into a ‘bundle’. For example if the data pipes “sphere”, “oblate spheroid”, “prolate spheroid”, and “ellipsoid” preexist, these can be grouped into a bundle called “diffusion tensors” with the following series of user function calls:

```
1 pipe.bundle(bundle='diffusion tensors', pipe='sphere')
2 pipe.bundle(bundle='diffusion tensors', pipe='oblate spheroid')
3 pipe.bundle(bundle='diffusion tensors', pipe='prolate spheroid')
4 pipe.bundle(bundle='diffusion tensors', pipe='ellipsoid')
```

The data pipe editor window of the GUI can also be used to bundle pipes together (see figure 1.12 on page 21).

4.2.2 Molecule, residue, and spin containers

Within a data pipe is the molecule, residue, and spin container data structure. Data which is specific to a given nucleus is stored in a special spin container structure. This includes relaxation data, model-free parameters, reduced spectral density mapping values, spin specific optimisation parameters, chemical shift tensor information, pseudo-contact shift values, etc. The spin containers can be created from 3D structural data or a sequence file, as described in the next two sections, or manually built.



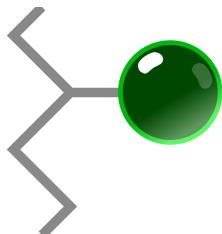
Molecule containers

The spin containers are part of a nested set of containers, and are graphically depicted in the spin viewer window of the GUI in figure 1.10 on page 20. As can be seen from the figure, the top level holds a single molecular container. Multiple molecular containers can be present if the study is of a molecular complex. Using the GUI menus or the prompt/scripting mode, molecule containers can be manually created with the user function:

```
1 molecule.create(mol_name='glycerol', mol_type='organic molecule')
```

In the spin viewer window of the GUI, right clicking on the “Spin system information” element will pop up a menu with an entry for adding molecule containers. Right clicking on molecule containers will show a pop up menu with an entry for permanently deleting the container.

Residue containers



Nested within the molecule containers are residue containers. These are graphically depicted in the spin viewer window (see figure 1.10 on page 20). Each molecule container can possess multiple residues. These require either a unique residue number or unique residue name. For organic molecules where the residue concept is meaningless, all spin containers can be held within a single unnamed and unnumbered residue container. Using the GUI menus or the prompt/scripting mode, residue containers can be manually created with the user function:

```
1 residue.create(res_num='-5', res_name='ASP')
```

Alternatively residues can be added in the spin viewer window from the pop up menu when right clicking on molecule containers, and can be deleted via the pop up menu when right clicking on the residue to delete.

Spin containers



Spin containers are nested within a residue container (again graphically depicted in the spin viewer window in figure 1.10 on page 20). Multiple spin containers can exist per residue. This allows, for example, a single model-free analysis simultaneously on the backbone nitrogen spins, side-chain tryptophan indole nitrogen spins and alpha carbon spins. Or, for example, studying the pseudocontact shifts for all nitrogen, carbon and proton spins in the molecule simultaneously.

Spin containers can be manually added via the `spin.create` user function in the GUI or prompt/scripting mode:

```
1 spin.create(spin_num='200', spin_name='NE1')
```

The spin viewer window can also be used by right clicking on residue containers.

Spin ID strings

Spins are often identified in relax using their ID strings. The spin ID strings follow the basic construct found in a number of other NMR software such as MOLMOL. The identification string is composed of three components:

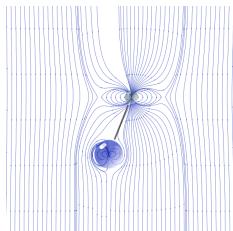
- The molecule ID token beginning with the “#” character,
- The residue ID token beginning with the “:” character,
- The atom or spin system ID token beginning with the “@” character.

Each token can be composed of multiple elements – one per spin – separated by the “,” character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the “–” character. Negative numbers are supported. The full ID string specification is “#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]”, where the token elements are “<mol_name>”, the name of the molecule, “<res_id>”, the residue identifier which can be a number, name, or range of numbers, “<atom_id>”, the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the “#” character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can, in some instances, be used to select spins. For example the string “@H*” will select the protons ‘H’, ‘H2’ and ‘H98’.

4.3 Interatomic data containers



Separate from the spin containers, yet strongly linked to them, are the interatomic data containers. These containers are grouped together within the same data pipe as the spins they point to. These define interactions between two spins located anywhere within the molecule, residue and spin nested data structure. These are automatically created when reading in data defined between two spins such as RDCs and NOE distance constraints. They can also be created using the `interatom.define` user function:

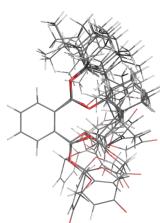
```
1 interatom.define(spin_id1=':2@N', spin_id2=':2@H')
```

As the interatomic data container concept is relatively new, how they are created and handled is likely to evolve and change in the future.

4.4 Setup in the prompt/script UI

Below are three different examples showing how to set up the relax data model for any analysis type requiring spin specific data.

4.4.1 Script mode – spins from structural data



3D structural data is stored at the level of the current data pipe. This data is completely separate from the molecule, residue and spin data structure. However the structural data can be used to generate the spin containers. For example for the nitrogen relaxation in a model-free analysis where both the nitrogen and proton are needed to define the magnetic dipole-dipole relaxation:

```
1 # Create a data pipe.
2 pipe.create(pipe_name='ellipsoid', pipe_type='mf')
3
4 # Load the PDB file.
5 structure.read_pdb('1f3y.pdb')
6
7 # Set up the 15N and 1H backbone spins.
```

```

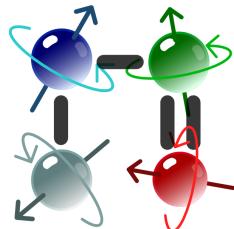
8  structure.load_spins('@N', ave_pos=True)
9  structure.load_spins('@H', ave_pos=True)
10
11 # Set up the 15N and 1H for the tryptophan indole ring.
12 structure.load_spins('@NE1', ave_pos=True)
13 structure.load_spins('@HE1', ave_pos=True)
14
15 # Define the spin isotopes.
16 spin.isotope('15N', spin_id='@N*')
17 spin.isotope('1H', spin_id='@H*')

```

The `structure.read_pdb` user function will load the structural data into the current data pipe, and the `structure.load_spins` user function will create the molecule, residue, and spin containers as needed. This will also load atomic position information into the matching spin containers. The `spin.isotope` user function is required to define the magnetic dipole-dipole interaction and is information not present in the PDB file.

Note that if structural data from the PDB is used to generate the spin containers, then all subsequent data loaded into relax must follow the exact naming convention from the PDB file. Automatic residue name matching (i.e. ‘GLY’ = ‘Gly’ = ‘gly’ = ‘G’) is currently not supported.

4.4.2 Script mode – spins from a sequence file



Alternatively to setting up the molecule, residue, and spin containers via 3D structural data, a plain text columnar formatted file can be used. This is useful for when no 3D structure exists for the molecule. It also has the advantage that the residue and atom names need not conform to the PDB standard. An example for reading sequence data is:

```

1 # Create a data pipe.
2 pipe.create(pipe_name='R1_1200', pipe_type='relax_fit')
3
4 # Set up the 15N spins.
5 sequence.read(file='noe.500.out', mol_name_col=1, res_num_col=2, res_name_col=3,
   spin_num_col=4, spin_name_col=5)
6 spin.element(element='N', spin_id='@N*')
7 spin.isotope('15N', spin_id='@N')

```

Here the molecule, residue, and spin information is extracted from the “`noe.500.out`” file which could look like:

# mol_name	res_num	res_name	spin_num	spin_name	value	error
Ap4Aase_new_3_mol1	1	GLY	1	N	None	None
Ap4Aase_new_3_mol1	2	PRO	11	N	None	None
Ap4Aase_new_3_mol1	3	LEU	28	N	None	None
Ap4Aase_new_3_mol1	4	GLY	51	N	0.03892194698453	0.01903177024613

Ap4Aase_new_3_mol1	5	SER	59	N	0.31240422567912	0.01859693729836
Ap4Aase_new_3_mol1	6	MET	71	N	0.42850831873249	0.0252585632304
Ap4Aase_new_3_mol1	7	ASP	91	N	0.53054928103134	0.02799062314416
Ap4Aase_new_3_mol1	8	SER	104	N	0.56528429775819	0.02170612146773
Ap4Aase_new_3_mol1	9	PRO	116	N	None	None
Ap4Aase_new_3_mol1	40	TRP	685	N	0.65394813490548	0.03830061886537
Ap4Aase_new_3_mol1	40	TRP	698	NE1	0.67073879732046	0.01426066343831

The file can contain columns for the molecule name, the residue name and number, and the spin name and number in any order though not all are needed. For example for a single protein system, the molecule name, residue name and spin number are nonessential. Or for an organic molecule, the molecule name, residue name and number and spin number could be nonessential. The subsequent user functions in the above example are used to set up the spin containers appropriately for a model-free analysis. These are not required in the automatic analysis of GUI as these user functions will be presented to you when adding relaxation data, or when clicking on the heteronucleus and proton buttons (“X isotope” and “H isotope”).

In the GUI, the creation of molecule, residue, and spin containers from a sequence file is also available via the “Load spins” wizard within the spin viewer window (*vide supra*).

4.4.3 Script mode – manual construction

For the masochists out there, the full molecule, residue and spin data structure can be manually constructed. For example:

```

1 # Manually create the molecule, residue, and spin containers.
2 molecule.create(mol_name='Ap4Aase', mol_type='protein')
3 residue.create(res_num=1, res_name='GLY')
4 residue.create(res_num=3, res_name='LEU')
5 residue.create(res_num=96, res_name='TRP')
6 spin.create(res_num=1, spin_name='N')
7 spin.create(res_num=3, spin_name='N')
8 spin.create(res_num=96, spin_name='N')
9 spin.create(res_num=96, spin_name='NE1')
```

These user functions can be repeated until the full sequence has been constructed.

4.5 Setup in the GUI

4.5.1 GUI mode – setting up the data pipe

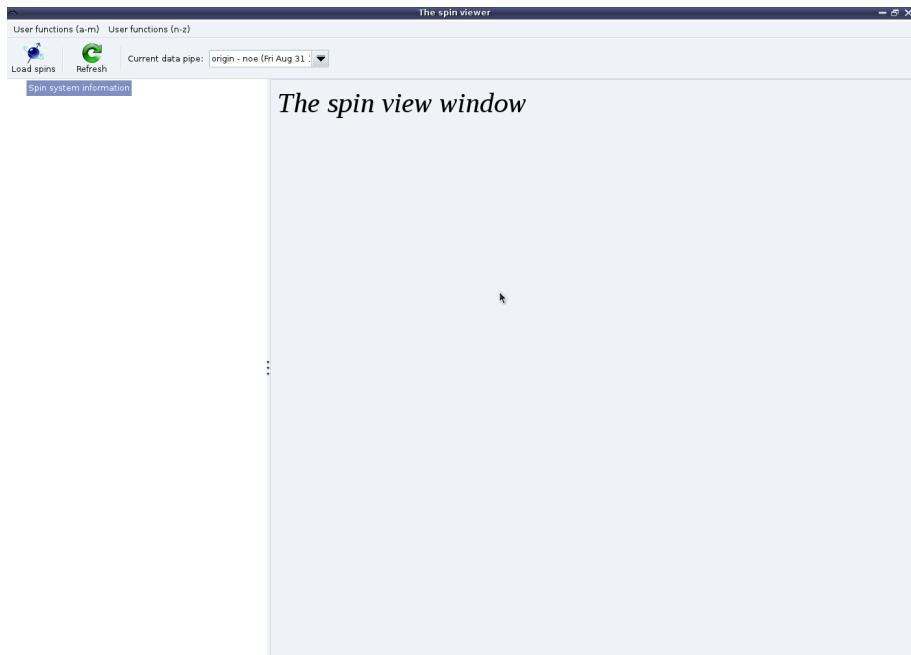
In the GUI, the most common way to create the data pipe is to initialise one of the auto-analyses via the analysis selection wizard (see Figure 1.4 on page 12). The initialisation will create the appropriate starting data pipe. Alternatively the data pipe editor can be used (see Figure 1.12 on page 21). Or the “User functions→pipe→create” menu item can be selected for graphical access to the `pipe.create` user function.

4.5.2 GUI mode – spins from structural data

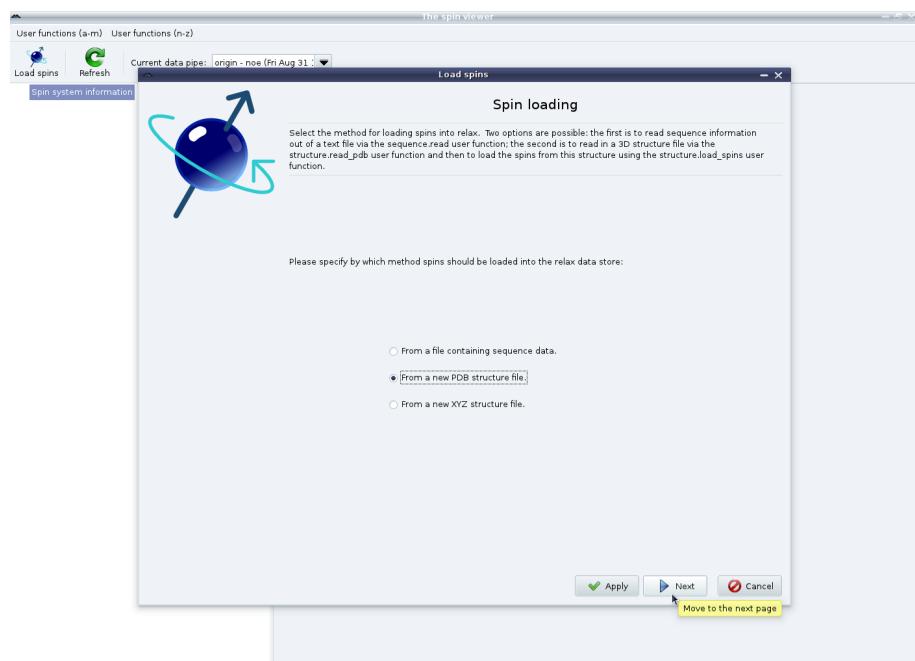
For this section, the example of protein ^{15}N relaxation data will be used to illustrate how to set up the data structures. To manipulate the molecule, residue and spin data structures in the GUI, the most convenient option is to use the spin viewer window (see Figure 1.10 on page 20). This window can be opened in four ways:

- The “View→Spin viewer” menu item,
- The “[Ctrl+T]” key combination,
- The spin viewer icon in the toolbar (represented by the blue spin icon),
- The “Spin editor” button part of the “Spin systems” GUI element in the specific analysis tabs.

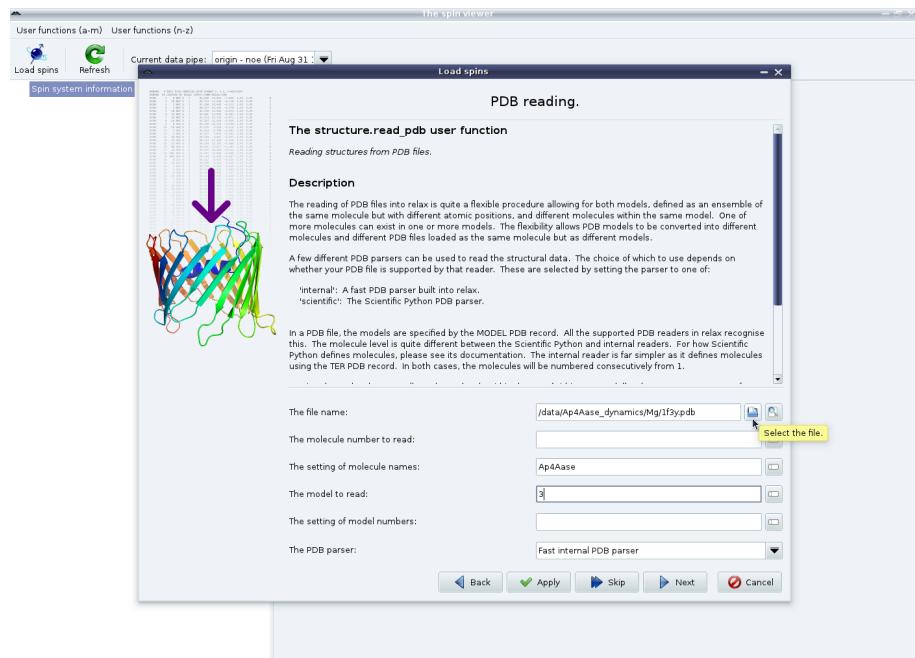
You will then see:



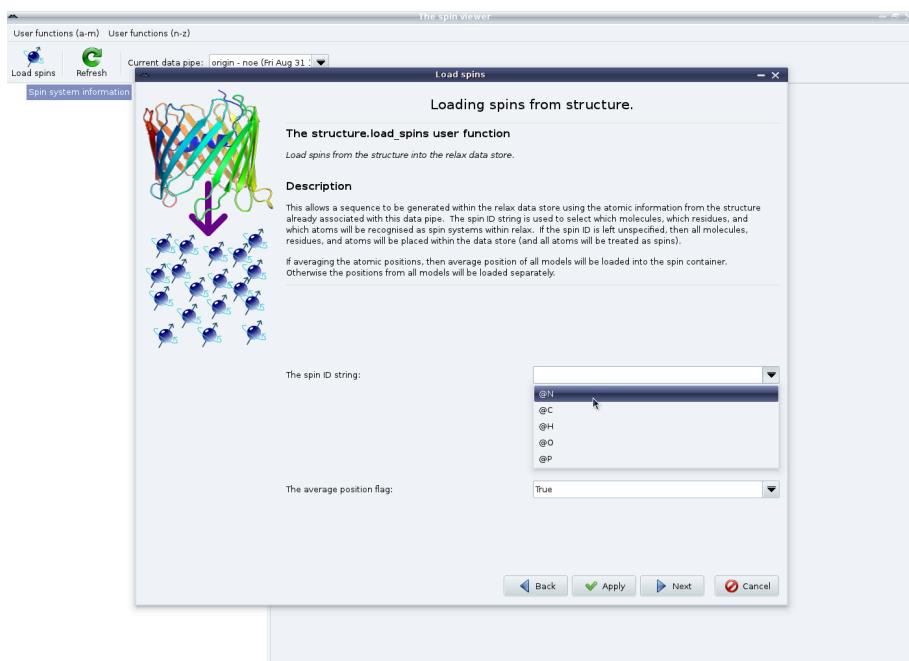
At this point, click on the “Load spins” button (or the “Load spins” menu entry from the right click pop up menu) to launch the spin loading wizard. A number of options will be presented to you:



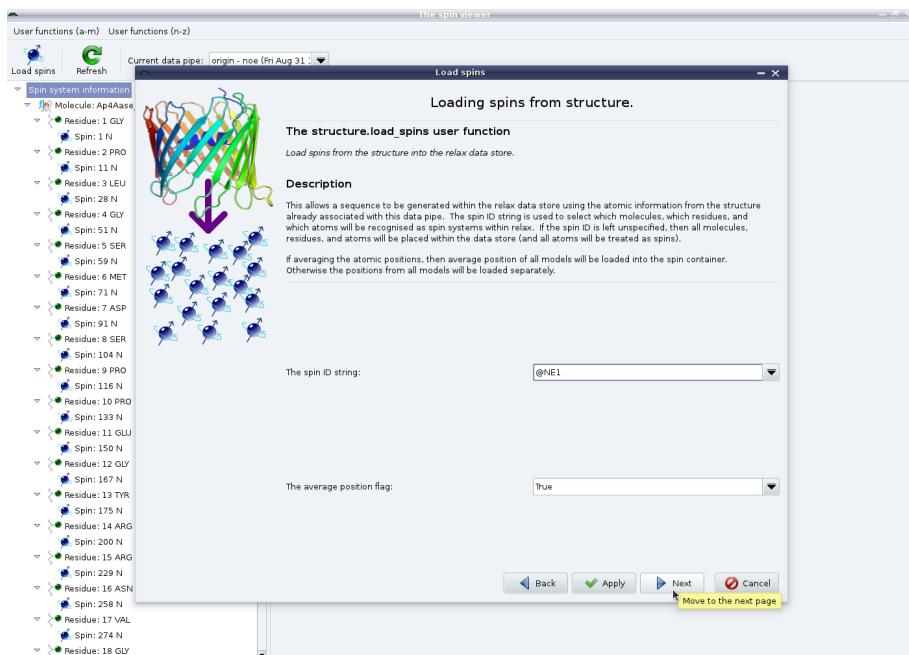
Here the spins will be loaded from a PDB file. If you do not have a 3D structure file, please see the next section. After selecting “From a new PDB structure file” and clicking on “Next”, you will see:



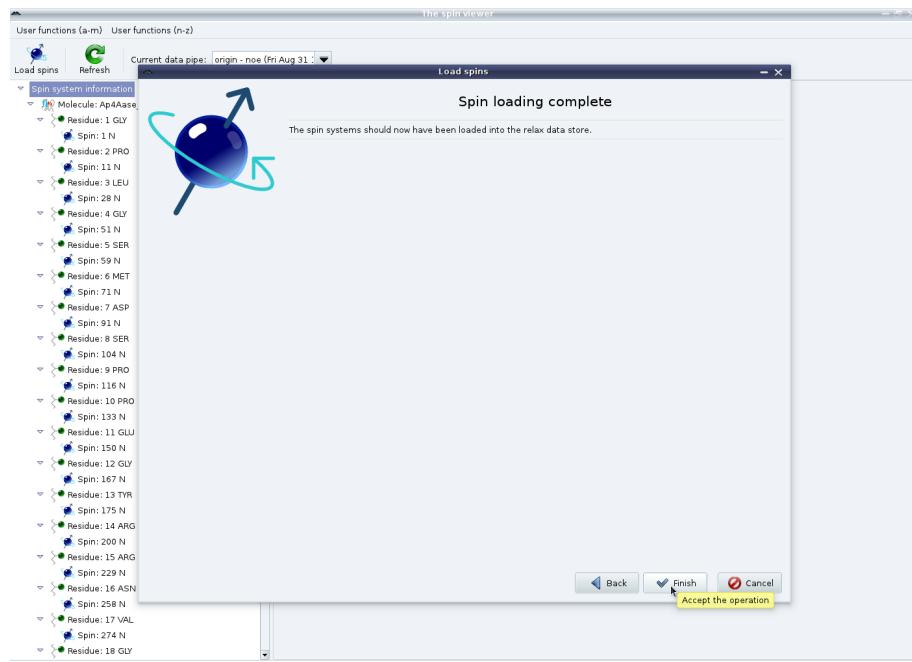
Now select the PDB file you wish to use. The other options in this screen allow you to handle NMR models and multiple molecules within a single PDB file. These options are explained in the window. Hovering the mouse over the options will give additional hints. In this example, the 3rd model from the 1F3Y PDB file will be read and the single molecule will be named “Ap4Aase” to override the default naming of “1f3y_mol1”. Now click on “Next” to bring up the spin loading page:



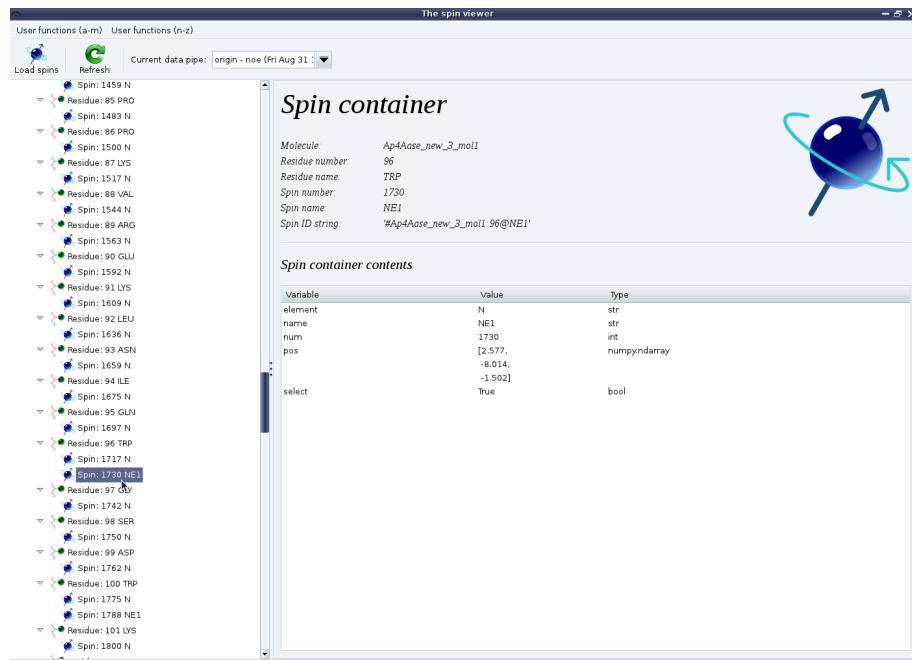
This is a bit more complicated. In this example we are studying the backbone dynamics of ^{15}N spins of a protein. Therefore first set the spin ID string to “@N” (which can be selected from the pull down) and click on “Apply” to set up the backbone spins. Do not click on “Next” yet. If the current study requires the specification of the dipole-dipole interaction (for example if it involves relaxation data – model-free analyses, consistency testing, reduced spectral density mapping; or the dipolar coupling – the N-state model or ensemble analyses, the Frame Order theory) you will also need to load the ^1H spins as well. Therefore set the spin ID string to “@H” and click on “Apply” again.



Now change the spin ID string to “@NE1” and then click on “Next” (or “Apply” if the Trp protons “@HE1” need to be loaded as well). This will add spin containers for the tryptophan indole ^{15}N spins. Finally click on “Finish” to exit the wizard:



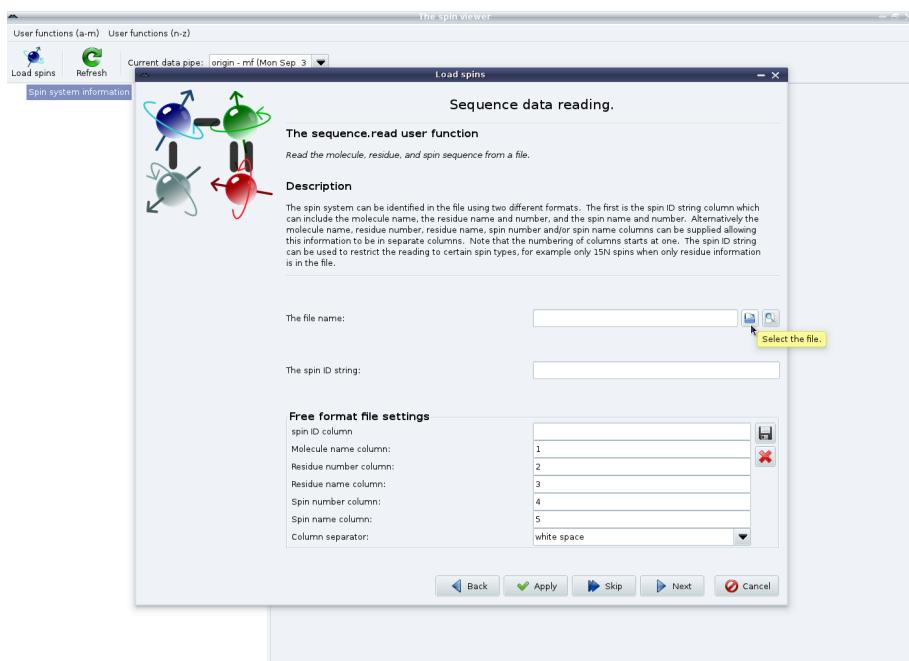
You should now see something such as:



If the ^1H spins have been loaded as well, then you should see exactly twice as many spin containers as shown above.

4.5.3 GUI mode – spins from a sequence file

Starting from the empty spin viewer window on page 40), click on the “Load spins” button. You will then see the spin loading wizard (see page 41). Select the option for reading data from a sequence file. You should then see:



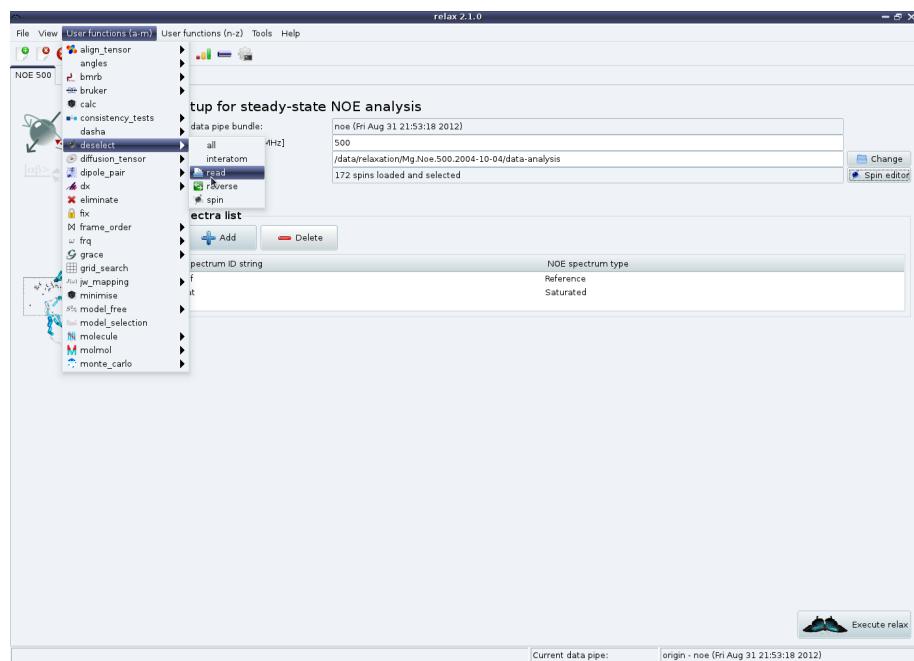
Select the file to load and change the “Free format file settings” as needed. An example of a suitable format is given on page [39](#). Click on “Next” to reach the wizard ending page (see [43](#)). Finally click on “Finish” to exit the wizard.

4.5.4 GUI mode – manual construction

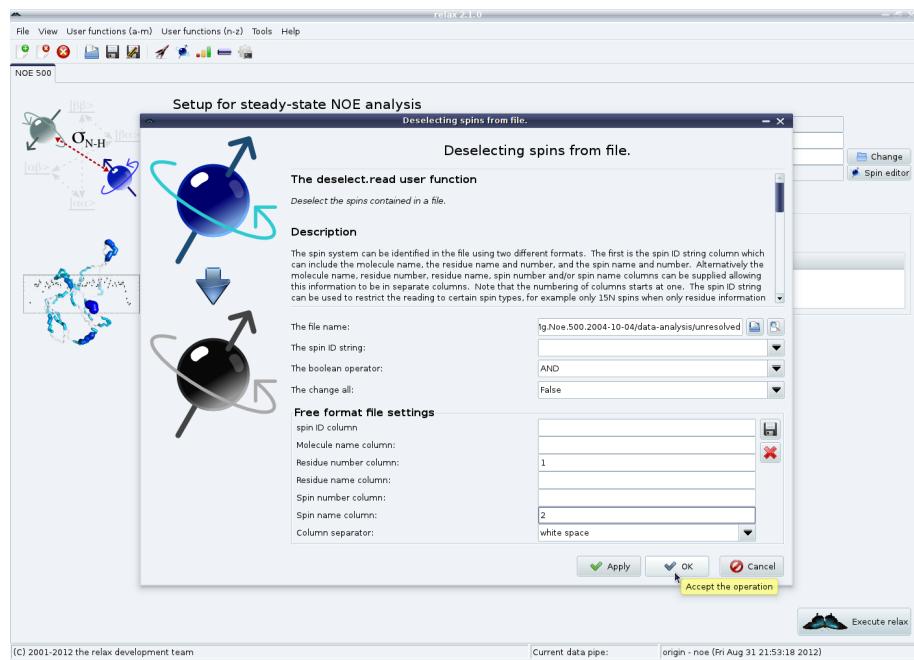
Just as in the prompt/script UI mode, the molecules, residues and spins can be manually added. First add a molecule by right clicking on the “Spin system information” element and selecting the relevant entry in the popup menu. Then right click on the newly created molecule container to add residues, and right click on residue containers to add spins.

4.5.5 GUI mode – deselect spins

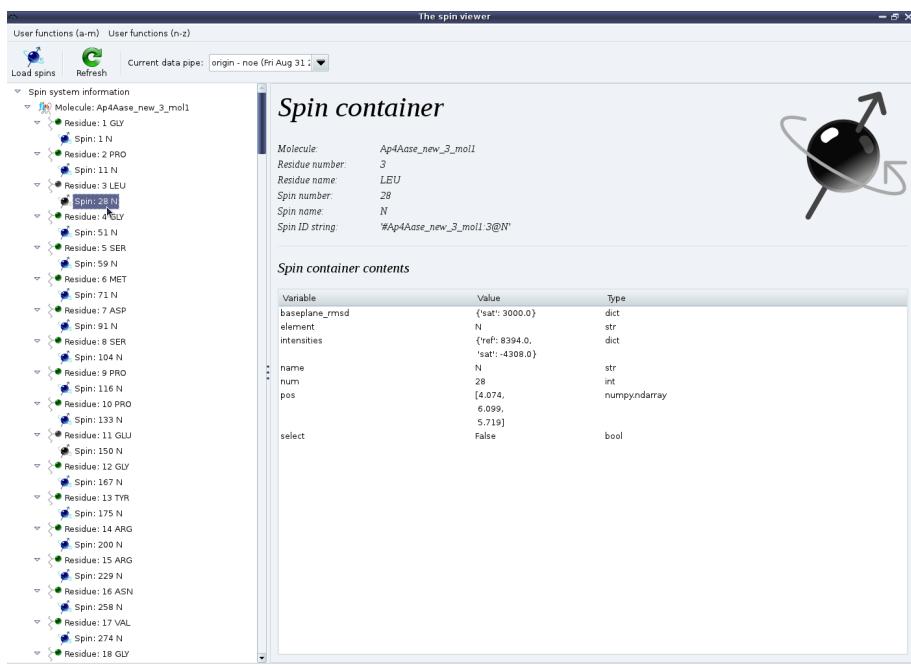
To deselect spins (for example if they are unresolved, overlapping peaks), click on the “User functions→deselect→read” menu item from the main relax window or the spin viewer window:



Select the file listing the unresolved spins and change the column numbers in the “Free format file settings” GUI element as needed:



Alternatively the spin editor window can be reopened and the spins manually deselected by right clicking on them and selecting “Deselect”. Returning to the spin editor window, you should now see certain spins coloured grey:



4.6 The next steps

This chapter presented the basics of setting up the relax data store, concepts which are needed for all analysis types built into relax. The next chapters will introduce specific analyses types – the steady-state NOE, R₁ and R₂ relaxation curve-fitting, and the automated full model-free analysis protocol of [d'Auvergne and Gooley \(2007, 2008b\)](#) – which build on the ideas introduced here.

Part II

The specific analyses

Chapter 5

The R_1 and R_2 relaxation rates – relaxation curve-fitting



5.1 Introduction to relaxation curve-fitting

The fitting of exponentials to relaxation curves (relaxation curve-fitting or as used throughout this chapter abbreviated simply as relax-fit) involves a number of steps including the loading of data, the calculation of both the average peak intensity across replicated spectra and the standard deviations of those peak intensities, selection of the experiment type, optimisation of the parameters of the exponential curves during the fit for each observed spin, Monte Carlo simulations to find the parameter errors, and saving and viewing the results. To simplify the process a sample script will be followed step by step as was done with the NOE calculation.

5.2 From spectra to peak intensities for the relaxation rates

The following subsections simply contain advice on how to go from the recorded FIDs to the peak lists ready to be input into relax. This need not be followed – it is simply a set of recommendations for obtaining the highest quality relaxation rates.

5.2.1 Temperature control and calibration



Before starting with the spectral processing, it should be noted that proper temperature control and calibration are essential for relaxation data. Small temperature changes can have an effect on the viscosity and hence global tumbling of the molecule being studied and, as the molecular diffusion tensor is the major contributor to relaxation, any non-consistent data will likely lead to artificial motions appearing in subsequent model-free analyses.

Per-experiment temperature calibration is essential and the technique used will need to be specified for BMRB data deposition. Note that the standard MeOH/ethylene glycol calibration of a spectrometer is of no use when you are running experiments which pump in large amounts of power into the probe head. Although the R1 experiment should be about the same temperature as a HSQC and hence be close to the standard MeOH/ethylene glycol spectrometer calibration, the R2 CPMG or spin lock and, to a lesser extent, the NOE pre-saturation pump a lot more power into the probe head. The power differences can either cause the temperature in the sample to be too high or too low. This is unpredictable as the thermometer used by the VT unit is next to the coils in the probe head and not inside the NMR sample. So the VT unit tries to control the temperature inside the probe head rather than in the NMR sample. However between the thermometer and the sample is the water of the sample, the glass of the NMR tube, the air gap where the VT unit controls air flow and the outside components of the probe head protecting the electronics. If the sample, the probe head or the VT unit is changed, this will have a different affect on the per-experiment temperature. The VT unit responds differently under different conditions and may sometimes over or under compensate by a couple of degrees. Therefore each relaxation data set from each spectrometer requires a per-experiment calibration.

Explicit temperature control techniques are also essential for relaxation data collection. Again the technique used will be asked for by relax for BMRB data deposition. A number of factors can cause significant temperature fluctuations between individual relaxation experiments. This includes the daily temperature cycle of the room housing the spectrometer, different amounts of power for the individual experiments, etc. The best methods for eliminating such problems are single scan interleaving and temperature compensation block. Single scan interleaving is the most powerful technique for averaging the temperature fluctuations not only across different experiments, but also across the entire measurement time. The application of off-resonance temperature compensation blocks at the start of the experiment is useful for the R2 and will normalise the temperature between the individual experiments, but single scan or single fid interleaving is nevertheless required for normalising the temperature across the entire measurement.

5.2.2 Spectral processing

For the best measurement of peak heights across the myriad of NMR spectral analysis software, it is recommend to zero fill a lot – 8k to 16k would give the best results. This does not increase the information content of the spectrum or decrease the errors, it simply interpolates. Even if the NMR spectral software performs 3-point quadratic interpolation

Table 5.1: Summary, First Point Scaling and Phase Correction

Delay	P1	FID	Spectrum
0 point	0	Scale -c 0.5	
1/2 point	180	Scale -c 1.0	Folded peaks have opposite sign
1 point	360	Scale -c 1.0	Use “POLY -auto -ord 0”

between the highest points to determine the peak height, the additional free interpolation will make the estimation more accurate.

Additionally, care must be taken to properly scale the first point as this can cause a baseline roll which will affect peak heights. A very useful description comes directly from the [NMRPipe manual](#):

Depending on the delay, the first point of the FID should be adjusted before Fourier Transform. The first point scaling factor is selected by the window function argument `-c`.

If the required first order phase P1 for the given dimension is 0.0, the first point scaling factor should be 0.5. This is because the discrete Fourier transform does the equivalent of counting the point at $t=0$ twice. If the first point is not scaled properly in this case, ridge-line baseline offsets in the spectrum will result.

In all other cases (P1 is not zero), this scale factor should be 1.0. This is because the first point of the FID no longer corresponds to $t=0$, and so it shouldn't be scaled. If the scale factor is not set correctly, it will introduce a baseline distortion which is either zero-order or sinusoidal, depending on what first-order phase is required. When possible, it is best to set up experiments with either exactly 0, 1/2, or 1-point delay. There are several reasons:

- Phase correction values can be determined easily.
- If the delay is not a multiple of 1/2 point, the phase of folded peaks will be distorted.
- The Hilbert transform (HT) is used, sometimes automatically, to reconstruct previously deleted imaginary data for interactive rephasing or inverse processing. But, the HT can only reconstruct imaginary data perfectly if the phase is a multiple of 1/2 point.
- Data with $P1 = 360$ have the first point $t=0$ missing (i.e. 1 point delay). Since the first point of the FID corresponds to the sum of points in the corresponding spectrum, this missing first point can be “restored” by adding a constant to the phased spectrum. This can be done conveniently by automated zero-order baseline correction, as shown in table 5.1.

Here is an example NMRPipe script designed for optimal relaxation rate extraction:

```

1 #!/bin/csh
2
3 setenv FILEROOT $1

```

```

4 set PHASE=81.4
5
6 echo "\n# Fourier Transform (nmrPipe fid/*.fid to ft/*.dat)"
7 echo "# t2 phase is set to $PHASE"
8 echo "# t1 phase is set to 0.0\n"
9
10 nmrPipe -in fid/$FILEROOT.fid \
| nmrPipe -fn SOL \
12 | nmrPipe -fn GM -g1 15 -g2 20 -c 0.5 \
13 | nmrPipe -fn ZF -size 8192 \
14 | nmrPipe -fn FT -auto \
15 | nmrPipe -fn PS -p0 $PHASE -p1 0.0 -di -verb \
16 | nmrPipe -fn TP \
17 | nmrPipe -fn SP -off 0.5 -end 0.98 -pow 2 -c 0.5 \
18 | nmrPipe -fn ZF -size 8192 \
19 | nmrPipe -fn FT -auto \
20 | nmrPipe -fn PS -p0 0.0 -p1 0.0 -di -verb \
21 | nmrPipe -fn TP \
22 | nmrPipe -fn POLY -auto \
23 | nmrPipe -fn EXT -left -sw \
24 | nmrPipe -out ft/$FILEROOT.dat -ov

```

The script is run by suppling the FILEROOT value as a command line option so if the script is called `nmrpipe.sh` and the `var2pipe` or `bruk2pipe` processed file `R1_ncyc4.fid` is in the `fid` directory, you would run:

```
$ ./nmrpipe.sh R1_ncyc4
```

The `ft` directory must exist for this script to execute. Different experiment specific options may be needed such as:

```
| nmrPipe -fn REV \
| nmrPipe -fn FT -neg \
| nmrPipe -fn PS -rs 2.5 \
```

The script should be changed for different phasing, first point scaling, a polynomial baseline correction added in the direct dimension or removed from the indirect dimension, solvent suppression removed or changed, and the window functions modified for optimal spectral quality. Each system and spectrum is different, so it is recommended that to find the optimal processing that each part of the script be removed and re-added one-by-one between processing and checking of the resultant spectrum. Note that the extraction at the end after the polynomial baseline correction in the indirect dimension is important as the baseline correction often displays a much better performance when the empty part of the spectrum is used in the calculation.

5.2.3 Measuring peak intensities

For the measurement of peak intensities, again care must be taken. A read of the paper:

- Viles, J., Duggan, B., Zaborowski, E., Schwarzinger, S., Huntley, J., Kroon, G., Dyson, H., and Wright, P. (2001). Potential bias in NMR relaxation data introduced by peak intensity analysis and curve fitting methods. *J. Biomol. NMR*, **21**, 1–9. ([10.1023/A:1011966718826](https://doi.org/10.1023/A:1011966718826))

is highly recommended. Despite the recommendations in the discussion of this paper, a different methodology using peak heights can be used to solve the same problems. This will be discussed in a paper which is currently in preparation from the Gooley group. The steps involved are:

- For the first spectrum in the time series, shift the peak list to the tops of the peaks (for example using “pc” in Sparky on subsets of peaks).
- Copy this 1st spectrum list onto all spectra, shifting the peaks to the top as in the previous step.
- When the peak disappears into the noise, leave it at its current position and do not type “pc” or equivalent. This will add weight to the first point in the subsequent step.
- Once all spectra are shifted, calculate an average peak list.
- Copy this average peak list onto fresh copies of all spectra.
- Measure peak heights using this averaged peak list.

This will produce the most accurate peak intensity measurements until better, more robust peak shape integration comes along. This is a special technique which is designed to minimise the white-noise bias talked about in the [Viles et al. \(2001\)](#) paper. As the noise often decreases with the decrease in total spectral power, using the tops of the peaks means that you are actually measuring the real peak height plus positive noise in all cases. This non-constant additional positive noise contribution can result in a double exponential in the measured data. The technique above eliminates this as you then measure close to real peak height with the addition of white noise centred at zero – it is both negative and positive to equal amounts – rather than the peak high with noise contribution strongly biased towards the positive. Where the peaks disappear, you then are measuring the pure baseplane noise. This is fine as these white-noise data points centred at zero will help in the subsequent exponential fit in relax.

If using Sparky then, to be sure that the peak heights are properly updated, for each spectrum type “pa” to select all peaks, “ph” to update all selected peak heights, “lt” to show the spectrum peaks window, make sure “data height” is selected in the options, and then save the peak list.

5.3 Relaxation curve-fitting in the prompt/script UI mode

5.3.1 Relax-fit script mode – the sample script

The following is a verbatim copy of the contents of the `sample_scripts/relax_fit.py` file. If your copy of the sample script is different than that below, please send an email to the relax-devel mailing list to tell the relax developers that the manual is out of date (see section [3.2.3](#) on page [30](#)). You will need to first copy this script to a dedicated analysis directory containing peak lists, a PDB file and a file listing unresolved spin systems, and then modify its contents to suit your specific analysis. The script contents are:

```

1 # Script for relaxation curve-fitting.
2
3 # Create the 'rx' data pipe.
4 pipe.create('rx', 'relax_fit')
5
6 # Load the backbone amide 15N spins from a PDB file.
7 structure.read_pdb('Ap4Aase_new_3.pdb')
8 structure.load_spins(spin_id='@N')
9 structure.load_spins(spin_id='@NE1')
10
11 # Spectrum names.
12 names = [
13     'T2_ncyc1_ave',
14     'T2_ncyc1b_ave',
15     'T2_ncyc2_ave',
16     'T2_ncyc4_ave',
17     'T2_ncyc4b_ave',
18     'T2_ncyc6_ave',
19     'T2_ncyc9_ave',
20     'T2_ncyc9b_ave',
21     'T2_ncyc11_ave',
22     'T2_ncyc11b_ave'
23 ]
24
25 # Relaxation times (in seconds).
26 times = [
27     0.0176,
28     0.0176,
29     0.0352,
30     0.0704,
31     0.0704,
32     0.1056,
33     0.1584,
34     0.1584,
35     0.1936,
36     0.1936
37 ]
38
39 # Loop over the spectra.
40 for i in range(len(names)):
41     # Load the peak intensities.
42     spectrum.read_intensities(file=names[i]+'.list', dir=data_path, spectrum_id=names[i],
43                               int_method='height')
44
45     # Set the relaxation times.
46     relax_fit.relax_time(time=times[i], spectrum_id=names[i])
47
48 # Specify the duplicated spectra.
49 spectrum.replicated(spectrum_ids=['T2_ncyc1_ave', 'T2_ncyc1b_ave'])
50 spectrum.replicated(spectrum_ids=['T2_ncyc4_ave', 'T2_ncyc4b_ave'])
51 spectrum.replicated(spectrum_ids=['T2_ncyc9_ave', 'T2_ncyc9b_ave'])
52 spectrum.replicated(spectrum_ids=['T2_ncyc11_ave', 'T2_ncyc11b_ave'])
53
54 # Peak intensity error analysis.
55 spectrum.error_analysis()
56
57 # Deselect unresolved spins.
58 deselect.read(file='unresolved', mol_name_col=1, res_num_col=2, res_name_col=3,
59               spin_num_col=4, spin_name_col=5)
59 # Set the relaxation curve type.

```

```

60 relax_fit.select_model('exp')
61
62 # Grid search.
63 grid_search(inc=11)
64
65 # Minimise.
66 minimise('simplex', scaling=False, constraints=False)
67
68 # Monte Carlo simulations.
69 monte_carlo.setup(number=500)
70 monte_carlo.create_data()
71 monte_carlo.initial_values()
72 minimise('simplex', scaling=False, constraints=False)
73 monte_carlo.error_analysis()
74
75 # Save the relaxation rates.
76 value.write(param='rx', file='rx.out', force=True)
77
78 # Save the results.
79 results.write(file='results', force=True)
80
81 # Create Grace plots of the data.
82 grace.write(y_data_type='chi2', file='chi2.agr', force=True)      # Minimised chi-squared
     value.
83 grace.write(y_data_type='i0', file='i0.agr', force=True)      # Initial peak intensity.
84 grace.write(y_data_type='rx', file='rx.agr', force=True)      # Relaxation rate.
85 grace.write(x_data_type='relax_times', y_data_type='intensities', file='intensities.agr',
     force=True)      # Average peak intensities.
86 grace.write(x_data_type='relax_times', y_data_type='intensities', norm=True, file='
     intensities_norm.agr', force=True)      # Average peak intensities (normalised).
87
88 # Display the Grace plots.
89 grace.view(file='chi2.agr')
90 grace.view(file='i0.agr')
91 grace.view(file='rx.agr')
92 grace.view(file='intensities.agr')
93 grace.view(file='intensities_norm.agr')
94
95 # Save the program state.
96 state.save('rx.save', force=True)

```

The next sections will break this script down into its logical components and explain how these parts will be interpreted by relax. To execute this script, please see section [1.2.8](#) on page [12](#) for details.

5.3.2 Relax-fit script mode – initialisation of the data pipe

The data pipe is simply created by the command

```

3 # Create the 'rx' data pipe.
4 pipe.create('rx', 'relax_fit')

```

This user function will then create a relaxation exponential curve-fitting specific data pipe labelled “rx”. The second argument sets the pipe type to that of the relaxation curve-fitting. Setting the pipe type is important so that the program knows which user functions are compatible with the data pipe, for example in the steady-state NOE analysis

the function `minimise` (see page 281) is meaningless as the NOE values are calculated directly rather than optimised.

5.3.3 Relax-fit script mode – setting up the spin systems

The first thing which needs to be completed prior to any spin specific command is to generate the molecule, residue and spin data structures for storing the spin specific data. In the sample script above this is generated from a PDB file, however a plain text file with the sequence information can be used instead (see the `sequence.read` user function on page 372 for more details). In the case of the sample script, the command

```
6 # Load the backbone amide 15N spins from a PDB file.
7 structure.read_pdb(name, 'Ap4Aase_new_3.pdb')
```

will load the PDB file `Ap4Aase_new_3.pdb` into relax. Then

```
8 structure.load_spins(spin_id='@N')
9 structure.load_spins(spin_id='@NE1')
```

will generate the molecule, residue, and spin sequence for the current data pipe. In this situation there will be a single spin system per residue generated corresponding to the backbone amide nitrogens as well as ^{15}N spins set up for the tryptophan indole nitrogens. Although the 3D coordinates have been loaded into the program from the PDB file, this structural information serves no purpose when calculating R_1 and R_2 values.

5.3.4 Relax-fit script mode – loading the data

To load the peak intensities into relax the `spectrum.read_intensities` and `relax_fit.relax_time` user functions are executed. Important keyword arguments for these user functions are the file name and directory, the spectrum identification string and the relaxation time period of the experiment in seconds. By default the file format will be automatically detected. Currently Sparky, XEasy, NMRView, and generic columnar formatted peak lists are supported. To be able to import any other type of format please send an email to the relax development mailing list with the details of the format. Adding support for new formats is trivial. The following series of commands – an expansion of the `for` loop in the sample script – will load peak intensities from six different relaxation periods, four of which have been duplicated, from Sparky peak lists with the peak heights in the 10th column.

```
spectrum.read_intensities('T2_ncyc1.list', spectrum_id='1', int_col=10)
relax_fit.relax_time(spectrum_id='1', time=0.0176)
spectrum.read_intensities('T2_ncyc1b.list', spectrum_id='1b', int_col=10)
relax_fit.relax_time(spectrum_id='1b', time=0.0176)
spectrum.read_intensities('T2_ncyc2.list', spectrum_id='2', int_col=10)
relax_fit.relax_time(spectrum_id='2', time=0.0352)
spectrum.read_intensities('T2_ncyc4.list', spectrum_id='4', int_col=10)
relax_fit.relax_time(spectrum_id='4', time=0.0704)
spectrum.read_intensities('T2_ncyc4b.list', spectrum_id='4b', int_col=10)
relax_fit.relax_time(spectrum_id='4b', time=0.0704)
spectrum.read_intensities('T2_ncyc6.list', spectrum_id='6', int_col=10)
relax_fit.relax_time(spectrum_id='6', time=0.1056)
spectrum.read_intensities('T2_ncyc9.list', spectrum_id='9', int_col=10)
```

```

relax_fit.relax_time(spectrum_id='9', time=0.1584)
spectrum.read_intensities('T2_ncyc9b.list', spectrum_id='9b', int_col=10)
relax_fit.relax_time(spectrum_id='9b', time=0.1584)
spectrum.read_intensities('T2_ncyc11.list', spectrum_id='11', int_col=10)
relax_fit.relax_time(spectrum_id='11', time=0.1936)
spectrum.read_intensities('T2_ncyc11b.list', spectrum_id='11b', int_col=10)
relax_fit.relax_time(spectrum_id='11b', time=0.1936)

```

The replicated spectra are set up with the commands

```

47 # Specify the duplicated spectra.
48 spectrum.replicated(spectrum_ids=['T2_ncyc1_ave', 'T2_ncyc1b_ave'])
49 spectrum.replicated(spectrum_ids=['T2_ncyc4_ave', 'T2_ncyc4b_ave'])
50 spectrum.replicated(spectrum_ids=['T2_ncyc9_ave', 'T2_ncyc9b_ave'])
51 spectrum.replicated(spectrum_ids=['T2_ncyc11_ave', 'T2_ncyc11b_ave'])

```

Note that the relaxation time period should be calculated directly from the pulse sequence (as the sum of delays and pulses for the period), as the estimated time may not match the real time. For the Sparky peak lists, by default relax assumes that the intensity value is in the 4th column. A typical file looks like:

Assignment	w1	w2	Data	Height
LEU3N-HN	122.454	8.397	129722	
GLY4N-HN	111.999	8.719	422375	
SER5N-HN	115.085	8.176	384180	
MET6N-HN	120.934	8.812	272100	
ASP7N-HN	122.394	8.750	174970	
SER8N-HN	113.916	7.836	218762	
GLU11N-HN	122.194	8.604	30412	
GLY12N-HN	110.525	9.028	90144	

By supplying the `int_col` argument to the `spectrum.read_intensities` user function, this can be changed. A typical XEasy file will look like:

No.	Color	w1	w2	ass. in w1	ass. in w2	Volume	Vol. Err.	Method	Comment
2	2	10.014	134.221	HN 21 LEU	N 21 LEU	7.919e+03	0.00e+00	m	
3	2	10.481	132.592	HE1 79 TRP	NE1 79 TRP	1.532e+04	0.00e+00	m	
17	2	9.882	129.041	HN 110 PHE	N 110 PHE	9.962e+03	0.00e+00	m	
18	2	8.757	128.278	HN 52 ASP	N 52 ASP	2.041e+04	0.00e+00	m	
19	2	10.086	128.297	HN 69 SER	N 69 SER	9.305e+03	0.00e+00	m	
20	3	9.111	127.707	HN 15 ARG	N 15 ARG	9.714e+03	0.00e+00	m	

where the peak height is in the `Volume` column. And for an NMRView file:

```

label dataset sw sf
H1 N15
cNTnC_noe0.nv
2505.63354492 1369.33557129
499.875 50.658000946
H1.L H1.P H1.W H1.B H1.E H1.J H1.U N15.L N15.P N15.W N15.B N15.E N15.J N15.U vol int stat comment flag0
0 {70.HN} 10.75274 0.02954 0.05379 ++ 0.0 {} {70.N} 116.37241 0.23155 0.35387 ++ 0.0 {} -6.88333129883 -0.1694 0 {} 0
1 {72.HN} 9.67752 0.03308 0.05448 ++ 0.0 {} {72.N} 126.41302 0.27417 0.37217 ++ 0.0 {} -5.49038267136 -0.1142 0 {} 0
2 {} 8.4532 0.02331 0.05439 ++ 0.0 {} 122.20137 0.38205 0.33221 ++ 0.0 {} -2.58034267191 -0.1320 0 {} 0

```

5.3.5 Relax-fit script mode – the rest of the setup

Once all the peak intensity data has been loaded a few calculations are required prior to optimisation. Firstly the peak intensities for individual spins needs to be averaged across replicated spectra. The peak intensity errors also have to be calculated using the standard deviation formula. These two operations are executed by the user function

```
53 # Peak intensity error analysis.  
54 spectrum.error_analysis()
```

Any spins which cannot be resolved due to peak overlap were included in a file called `unresolved`. This file can consist of optional columns of the molecule name, the residue name and number, and the spin name and number. The matching spins are excluded from the analysis by the user function

```
56 # Deselect unresolved spins.  
57 deselect.read(file='unresolved', mol_name_col=1, res_num_col=2, res_name_col=3,  
    spin_num_col=4, spin_name_col=5)
```

Finally the experiment type is specified by the command

```
59 # Set the relaxation curve type.  
60 relax_fit.select_model('exp')
```

The argument “`exp`” sets the relaxation curve to a two parameter $\{R_x, I_0\}$ exponential which decays to zero. The formula of this function is

$$I(t) = I_0 e^{-R_x \cdot t}, \quad (5.1)$$

where $I(t)$ is the peak intensity at any time point t , I_0 is the initial intensity, and R_x is the relaxation rate (either the R_1 or R_2). Changing the user function argument to “`inv`” will select the inversion recovery experiment. This curve consists of three parameters $\{R_1, I_0, I_\infty\}$ and does not decay to zero. The formula is

$$I(t) = I_\infty - I_0 e^{-R_1 \cdot t}. \quad (5.2)$$

5.3.6 Relax-fit script mode – optimisation of exponential curves

Now that everything has been setup minimisation can be used to optimise the parameter values. Firstly a grid search is applied to find a rough starting position for the subsequent optimisation algorithm. Eleven increments per dimension of the model (in this case the two dimensions $\{R_x, I_0\}$) is sufficient. The user function for executing the grid search is

```
62 # Grid search.  
63 grid_search(inc=11)
```

The next step is to select one of the minimisation algorithms to optimise the model parameters. Currently for relaxation curve-fitting only simplex minimisation is supported. This is because the relaxation curve-fitting C module is incomplete only implementing the chi-squared function. The chi-squared gradient (the vector of first partial derivatives) and chi-squared Hessian (the matrix of second partial derivatives) are not yet implemented in the C modules and hence optimisation algorithms which only employ function calls are

supported. Simplex minimisation is the only technique in relax which fits this criterion. In addition constraints cannot be used as the constraint algorithm is dependent on gradient calls. Therefore the minimisation command for relaxation curve-fitting is forced to be

```
65 # Minimise.
66 minimise('simplex', constraints=False)
```

5.3.7 Relax-fit script mode – error analysis

Only one technique adequately estimates parameter errors when the parameter values were found by optimisation – Monte Carlo simulations. In relax this can be implemented by using a series of functions from the `monte_carlo` user function class. Firstly the number of simulations needs to be set

```
68 # Monte Carlo simulations.
69 monte_carlo.setup(number=500)
```

For each simulation, randomised relaxation curves will be fit using exactly the same methodology as the original exponential curves. These randomised curves are created by back calculation from the fitted model parameter values and then each point on the curve randomised using the error values set earlier in the script

```
70 monte_carlo.create_data()
```

As a grid search for each simulation would be too computationally expensive, the starting point for optimisation for each simulation can be set to the position of the optimised parameter values of the model

```
71 monte_carlo.initial_values()
```

Then exactly the same optimisation as was used for the model can be performed

```
72 minimise('simplex', constraints=False)
```

The parameter errors are then determined as the standard deviation of the optimised parameter values of the simulations

```
73 monte_carlo.error_analysis()
```

5.3.8 Relax-fit script mode – finishing off

To finish off, the script first saves the relaxation rates together with their errors in a simple text file

```
75 # Save the relaxation rates.
76 value.write(param='rx', file='rx.out', force=True)
```

Grace plots are created and viewed

```
81 # Create Grace plots of the data.
82 grace.write(y_data_type='chi2', file='chi2.agr', force=True)      # Minimised chi-squared
83           value.
84 grace.write(y_data_type='i0', file='i0.agr', force=True)        # Initial peak intensity.
```

```
84 grace.write(y_data_type='rx', file='rx.agr', force=True)      # Relaxation rate.  
85 grace.write(x_data_type='relax_times', y_data_type='intensities', file='intensities.agr',  
     force=True)      # Average peak intensities.  
86  
87 grace.write(x_data_type='relax_times', y_data_type='intensities', norm=True, file='  
     intensities_norm.agr', force=True)      # Average peak intensities (normalised).
```

and viewed

```
88 # Display the Grace plots.  
89 grace.view(file='chi2.agr')  
90 grace.view(file='i0.agr')  
91 grace.view(file='rx.agr')  
92 grace.view(file='intensities.agr')  
93 grace.view(file='intensities_norm.agr')
```

and finally the program state is saved for future reference

```
95 # Save the program state.  
96 state.save(file='rx.save', force=True)
```

5.4 The relaxation curve-fitting auto-analysis in the GUI

The R_1 and R_2 relaxation rates can be calculated using the relax GUI (see Figures 1.6 and 1.7). These auto-analyses can be selected using the analysis selection wizard (Figure 1.4 on page 12). Just as with the steady-state NOE in the next chapter, these auto-analyses are very similar in spirit to the sample script described in this chapter, though the Grace 2D visualisation is more advanced. If you have read this chapter, the usage of these analyses should be self explanatory.

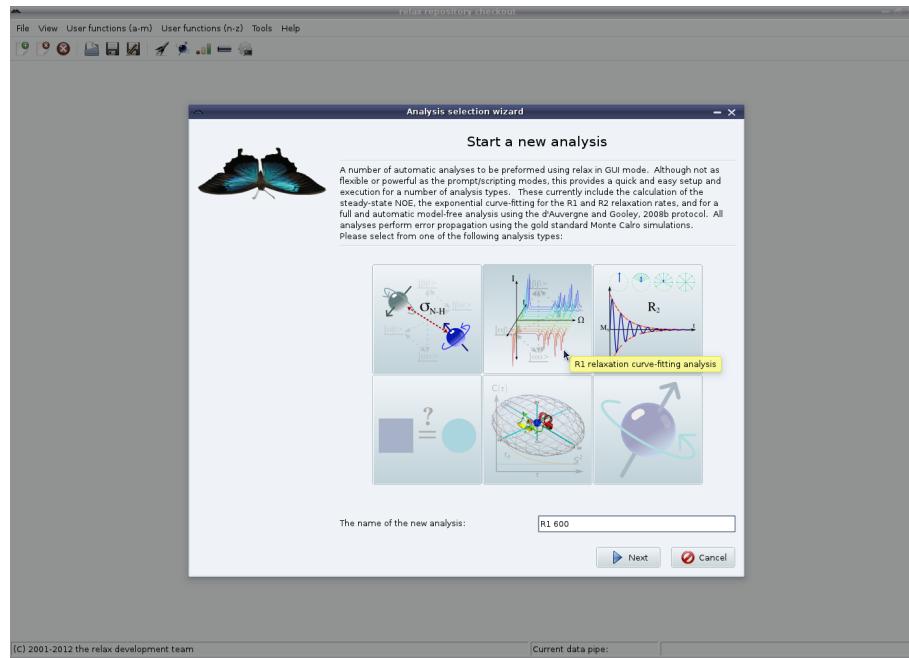
As in the script/prompt UI section above, the example of protein ^{15}N R_1 relaxation analysis will be performed in the following sections. To keep track of all the messages relax produces for future reference, you can run the relax GUI with the following command line arguments:

```
$ relax --log log --gui
```

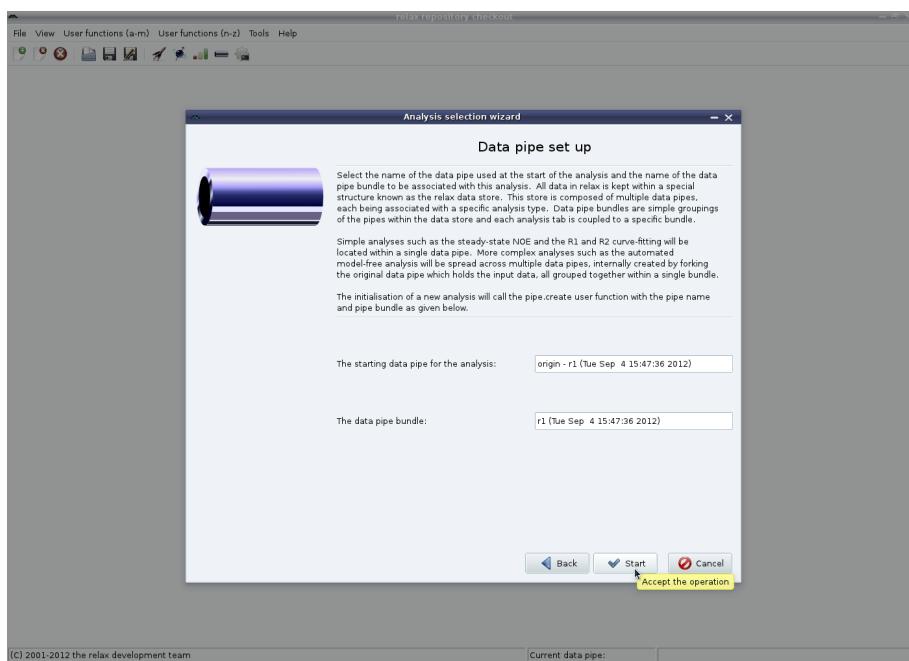
The messages will then appear both in the relax controller window (see Figure 1.9 on page 19) and in the `log` file.

5.4.1 Relax-fit GUI mode – initialisation of the data pipe

To begin the analysis, launch the analysis selection wizard (see Figure 1.4 on page 12). Select either the R_1 or R_2 analyses, and change the name of the analysis if you plan on running multiple analyses from different field strengths in one relax instance.

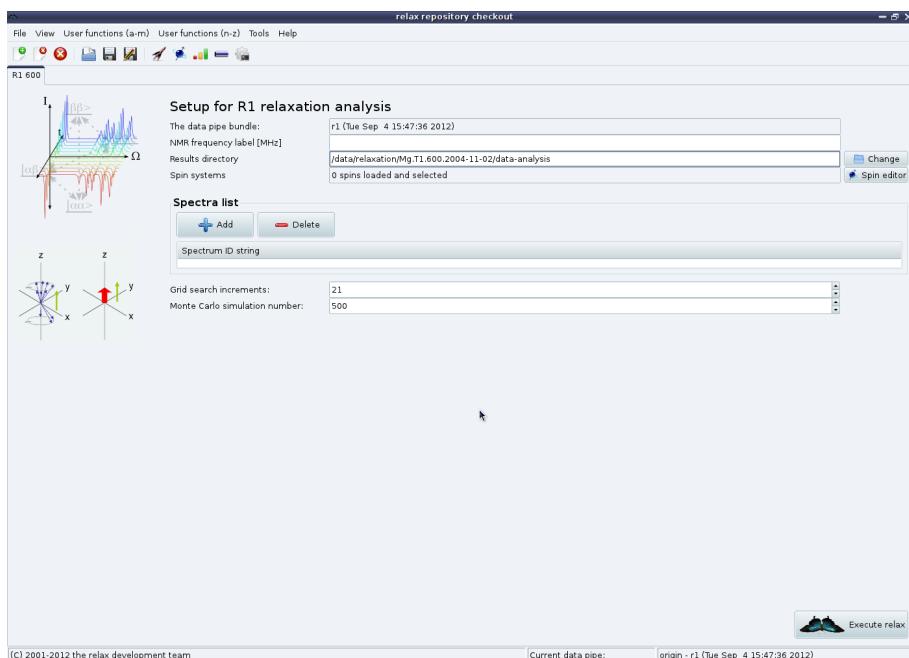


Then click on the “Next” button. On the second page click on “Start” to commence the analysis – this second part of the wizard does not need to be changed. For the R_1 and R_2 analyses in the GUI, a data pipe bundle containing only a single data pipe for that analysis will be created. This data pipe bundle can be safely ignored.



5.4.2 Relax-fit GUI mode – general setup

You will now be presented with a blank analysis tab:



Here there are two things unique to the GUI which need to be preformed:

NMR frequency label: First set the NMR frequency label. This is only used for the name of the output file. For example if you set the label to “1200”, the file `r1.1200.out` will be created at the end of the analysis.

Results directory: All of the automatically created results and Grace files will be placed into this directory. The “Results directory” can now be changed.

5.4.3 Relax-fit GUI mode – setting up the spin systems

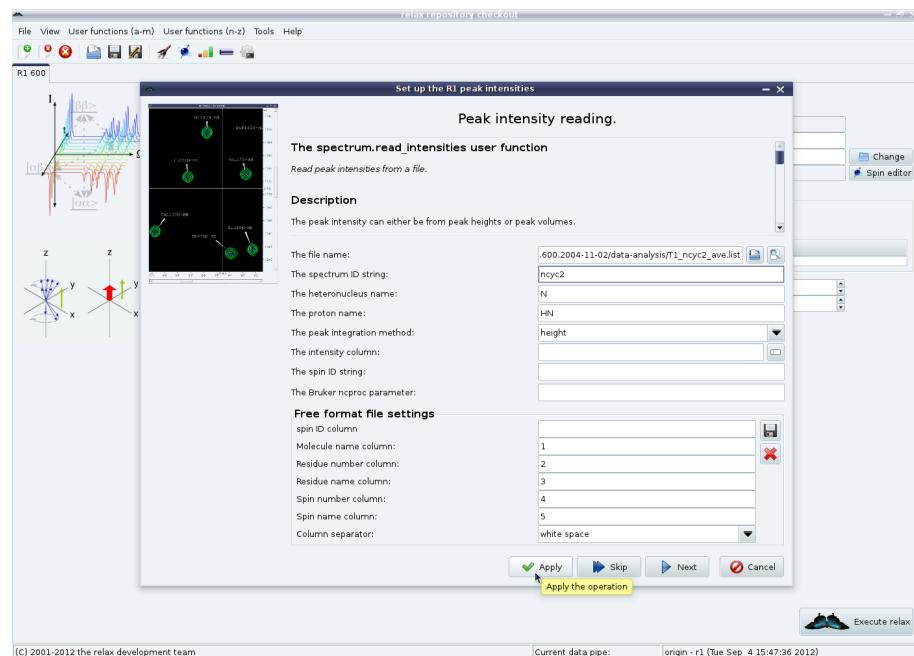
As the relaxation data is at the level of the spins, the molecule, residue and spin data structures need to be set up. In the R₁ and R₂ GUI analysis tabs, there is a special “Spin systems” GUI element designed for this. This will initially say “0 spins loaded and selected”. Click on the “Spin editor” button to launch the spin viewer window. The steps for setting up the spin containers using PDB files are described in section 4.5.2 on page 40 or for sequence files in section 4.5.3 on page 43.

5.4.4 Relax-fit GUI mode – unresolved spins

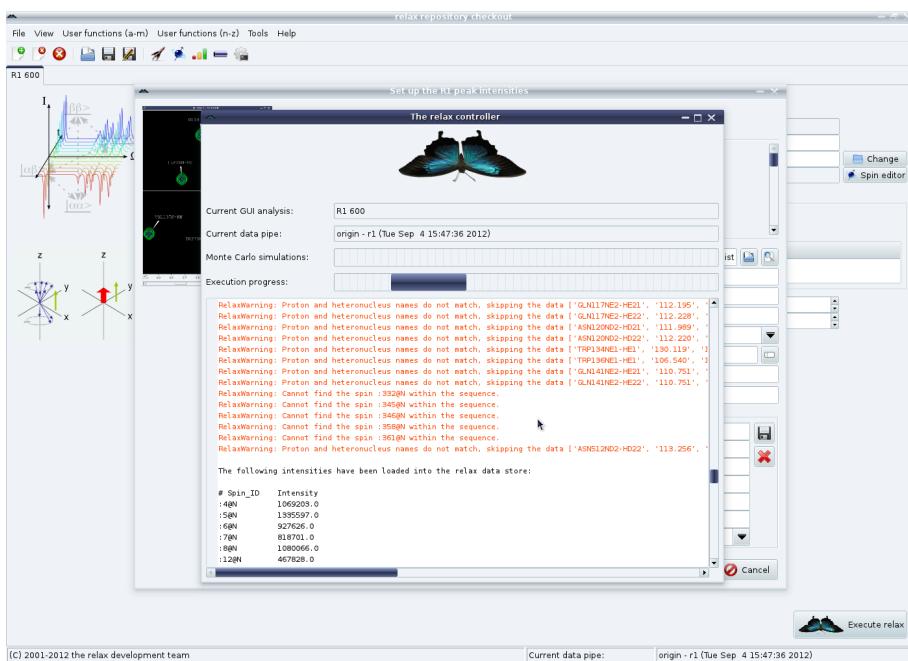
As in the prompt/script UI section 5.3.5, the spins can be deselected at this point using the same **unresolved** file. This is described in detail in section 4.5.5 on page 44.

5.4.5 Relax-fit GUI mode – loading the data

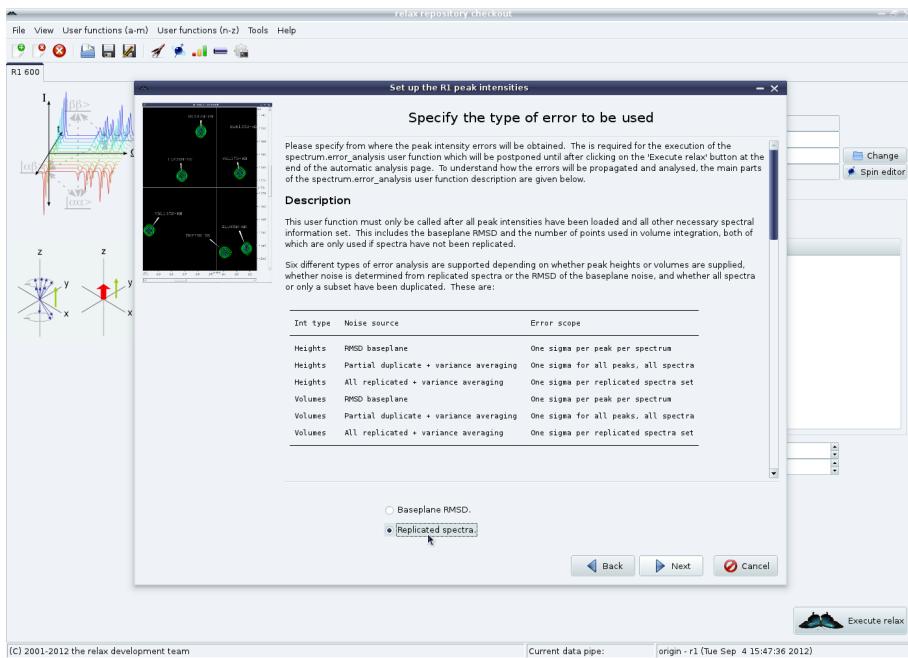
At this stage, the peak intensity data needs to be loaded. In both the R₁ and R₂ analysis tabs is a “Spectra list” GUI element. Click on the “Add” button to launch the peak intensity loading wizard:



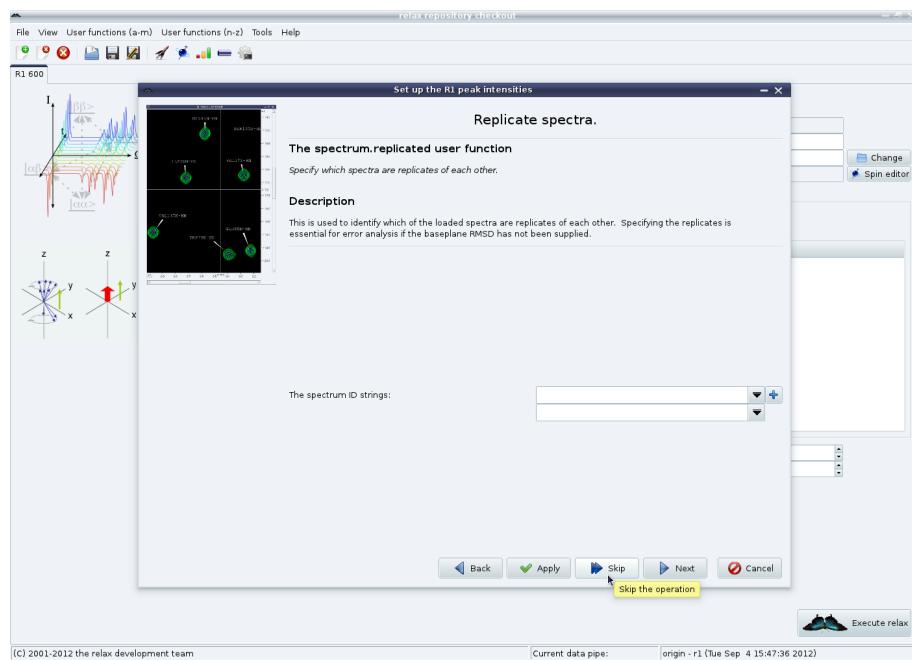
In this example, a Sparky peak list containing the peak heights determined from the averaged chemical shift positions for all spectra will be loaded. Set the spectrum ID string to a unique value. Click on “Next”. This will most likely cause a **RelaxWarning** message to appear for all peak list elements which do not correspond to any spins loaded into the relax data store:



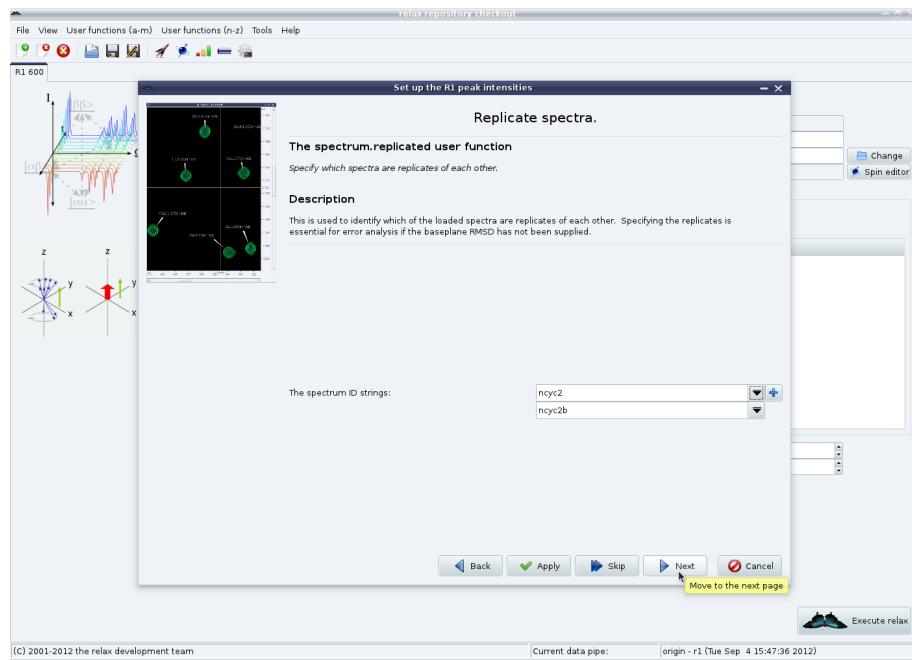
These messages must be carefully checked to be sure that the correct data has been loaded. A `RelaxError` might be thrown if the peak list is corrupted or if the dimension has been incorrectly given. In this case check the message, go “Back”, fix the problem, and click on “Next” again. Then click on “Next”. You should now see the error type page:



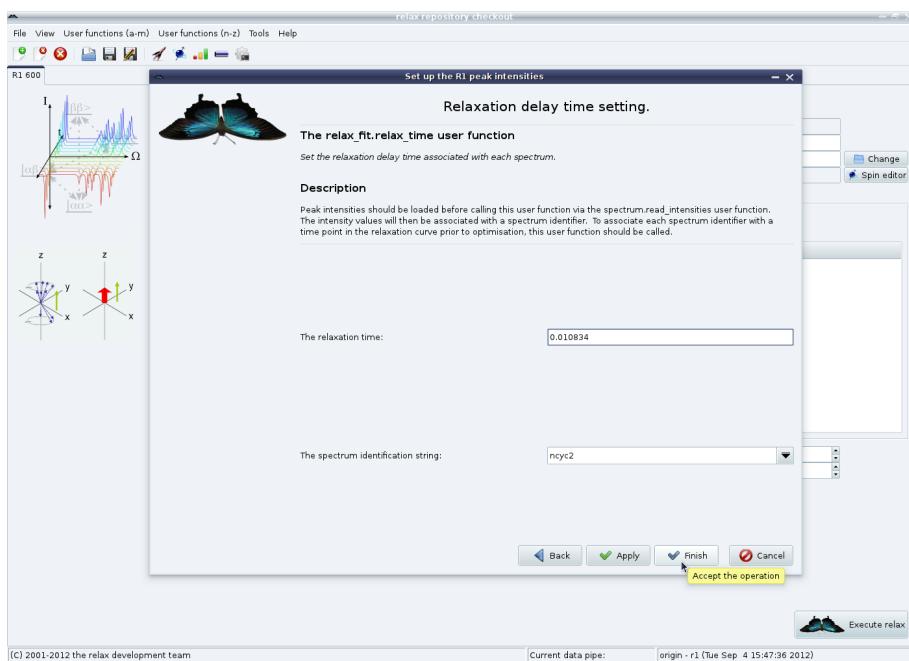
The description for this wizard page should be very carefully read – it will tell you about all of the error analysis options available and how these are implemented in relax. For the protein relaxation example, replicated spectra have been collected. Therefore the option “Replicated spectra” will be chosen. The “Baseplane RMSD” option is documented in the NOE chapter. After clicking on “Next” you will see:



For the first of the duplicate spectra, or any spectrum without a duplicate, you can click on the “Skip” button. If this is the second spectrum you have loaded from a duplicated set, select the two replicated spectra and then click on “Next”:

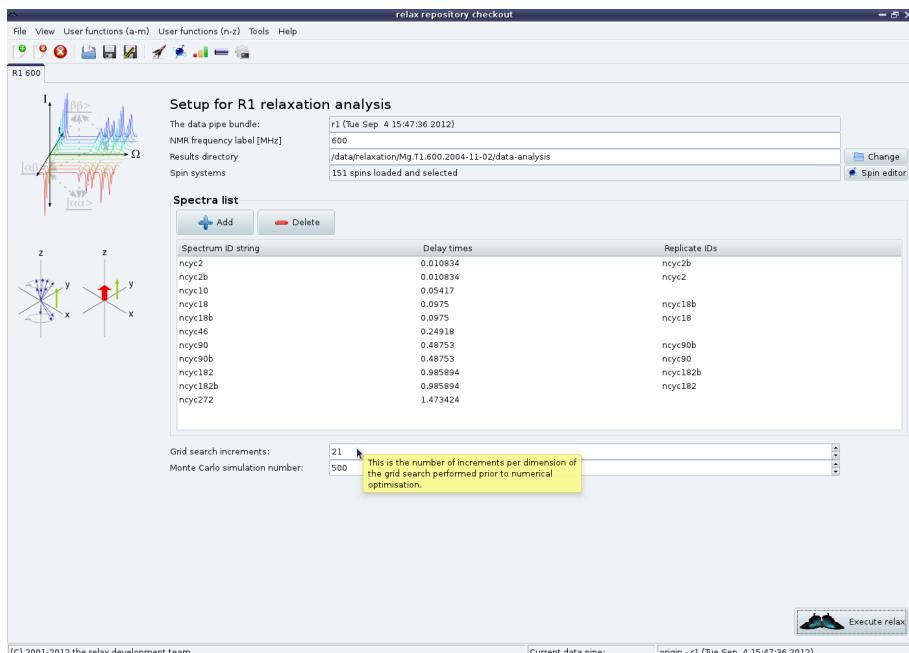


Finally set the relaxation time period for this experiment in seconds:



All delays and pulse lengths in the pulse sequence should be carefully checked to be sure that the time is exactly what you would expect – the estimated time may not match the real time. To set the time and close the wizard, click on the “Finish” button.

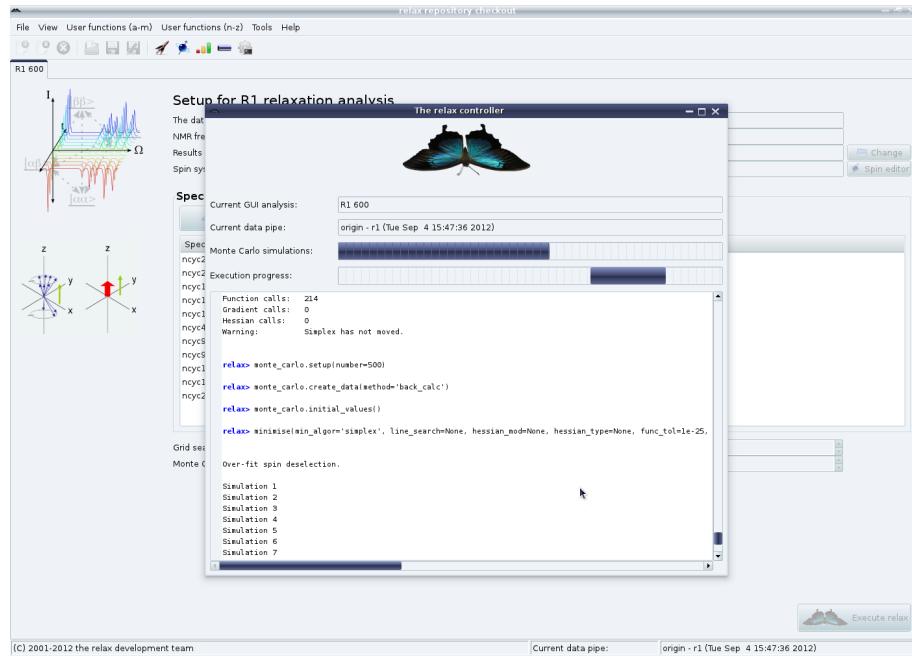
This procedure should be repeated for every experiment you have collected (you could, as an alternative, load all at the same time using the “Apply” button at each stage). In the end you should see something such as:



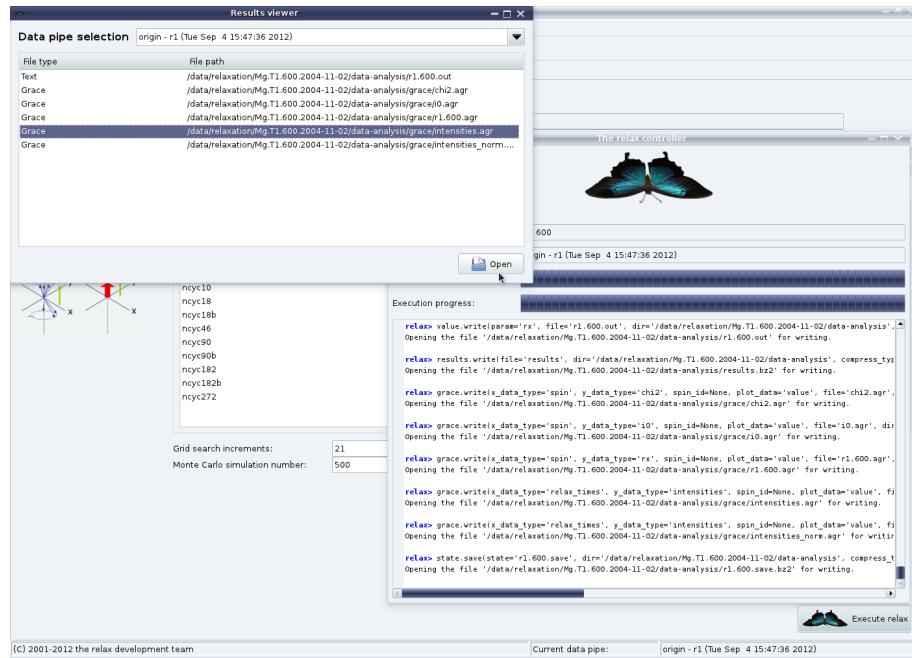
5.4.6 Relax-fit GUI mode – optimisation and error analysis

Back in the main R_1 analysis tab, the grid search increments and number of Monte Carlo simulations can be changed. The default values of 21 grid search increments and 500 MC

simulations are optimal – lower values are not recommended. To perform the optimisation and error analysis, click on the “Execute relax” button. The relax controller will open to show you the progress of the optimisation and simulations:



Once finished, the “Results viewer” window will also appear:



This window can be used to open the text files in the default text editor for your operating system or the 2D Grace plots in **xmgrace** if available on your system.

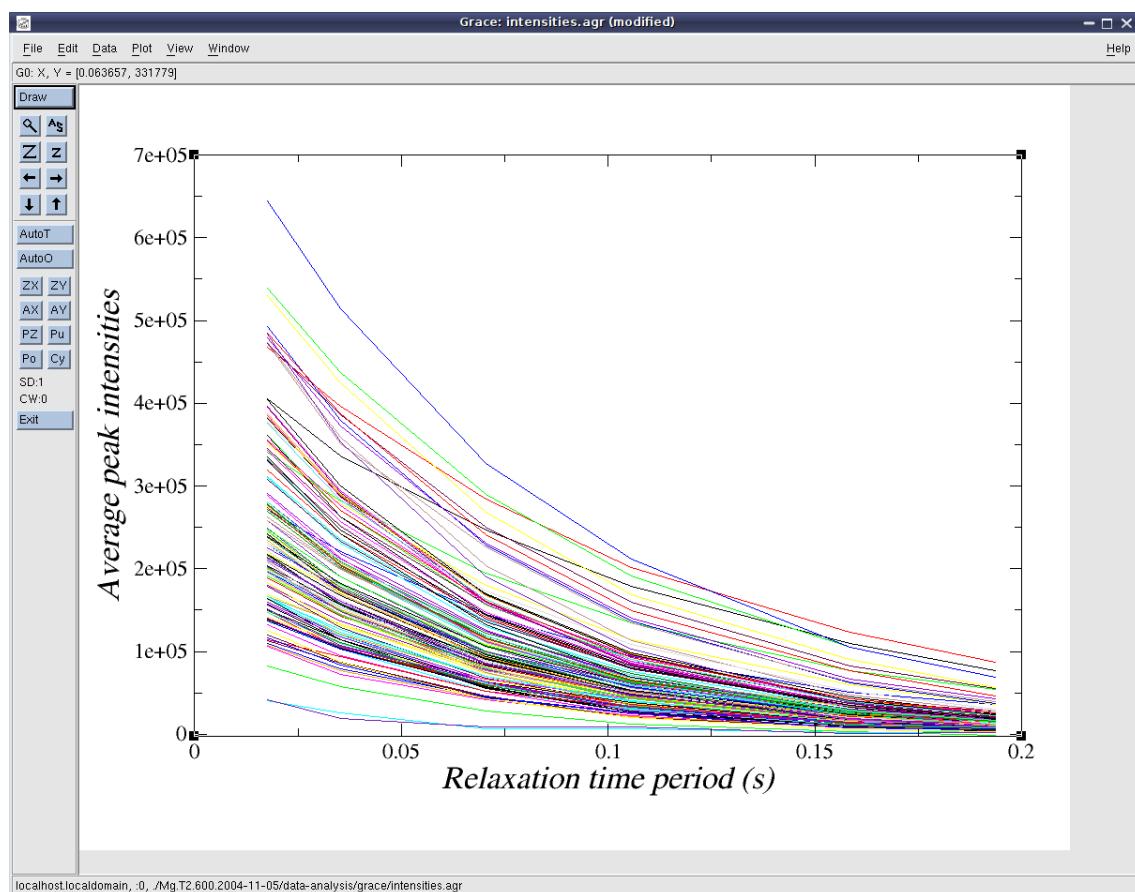


Figure 5.1: Screenshot of the 2D peak intensity plots for the exponential relaxation curves in Xmgrace.

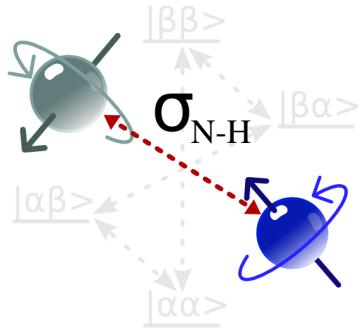
5.5 Final checks of the curve-fitting

To be sure that the data has been properly collected and that no instrumentation or pulse sequence timing errors have occurred, it is essential to carefully check the `intensities.agr` and `intensities_norm.agr` 2D Grace files. These are plots of the decay curves for each spin system analysed, and any non-exponential behaviour should be clearly visible (see Figure 5.1). If Xmgrace or a compatible program is not available for your operating system, the Grace files contain text representations of the curves at the end which can be opened, edited and visualised in any another 2D graphing software package.

Note that errors resulting in systematic bias in the data – for example if temperature control (single-scan interleaving or temperature compensation blocks) or per-experiment/per-spectrometer temperature calibration on MeOH or ethylene glycol have not been performed – will not be detected by looking at the decay curves. See section 5.2.1 or the `relax_data.temp_calibration` user function documentation on page 356 and the `relax_data.temp_control` user function documentation on page 357 for more details.

Chapter 6

Calculating the NOE



6.1 Introduction to the steady-state NOE

The calculation of NOE values is a straight forward and quick procedure which involves two components – the calculation of the value itself and the calculation of the errors. To understand the steps involved the execution of a sample NOE calculation script will be followed in detail. Then the same operations will be presented for the perspective of the graphical user interface.

6.2 From spectra to peak intensities for the NOE

For a set of recommendations for how to obtain the best quality relaxation rates, please see section 5.2 on page 49. In summary the following are important – temperature control (though the standard steady-state NOE single FID interleaved pulse sequences are fine), per-experiment temperature calibration, spectral processing with massive zero-filling and no baseplane rolling, and using an averaged peak list for determining the peak heights.

6.3 Calculation of the NOE in the prompt/script UI mode

6.3.1 NOE script mode – the sample script

This sample script can be found in the `sample_scripts` directory and will be used as the template for the next sections describing how to use relax.

```

1 # Script for calculating NOEs.
2
3 # Create the data pipe.
4 pipe.create('NOE', 'noe')
5
6 # Load the sequence from a PDB file.
7 structure.read_pdb('Ap4Aase_new_3.pdb')
8 structure.load_spins(spin_id='@N')
9 structure.load_spins(spin_id='@NE1')
10
11 # Load the reference spectrum and saturated spectrum peak intensities.
12 spectrum.read_intensities(file='ref.list', spectrum_id='ref_ave')
13 spectrum.read_intensities(file='sat.list', spectrum_id='sat_ave')
14
15 # Set the spectrum types.
16 noe.spectrum_type('ref', 'ref_ave')
17 noe.spectrum_type('sat', 'sat_ave')
18
19 # Set the errors.
20 spectrum.baseplane_rmsd(error=3600, spectrum_id='ref_ave')
21 spectrum.baseplane_rmsd(error=3000, spectrum_id='sat_ave')
22
23 # Individual residue errors.
24 spectrum.baseplane_rmsd(error=122000, spectrum_type='ref', res_num=114)
25 spectrum.baseplane_rmsd(error=8500, spectrum_type='sat', res_num=114)
26
27 # Peak intensity error analysis.
28 spectrum.error_analysis()
29
30 # Deselect unresolved spins.
31 deselect.read(file='unresolved', res_num_col=1, spin_name_col=2)
32
33 # Calculate the NOEs.
34 calc()
35
36 # Save the NOEs.
37 value.write(param='noe', file='noe.out', force=True)
38
39 # Create Grace files.
40 grace.write(y_data_type='ref', file='ref.agr', force=True)
41 grace.write(y_data_type='sat', file='sat.agr', force=True)
42 grace.write(y_data_type='noe', file='noe.agr', force=True)
43
44 # View the Grace files.
45 grace.view(file='ref.agr')
46 grace.view(file='sat.agr')
47 grace.view(file='noe.agr')
48
49 # Write the results.
50 results.write(file='results', dir=None, force=True)
51
52 # Save the program state.

```

```
53 state.save('save', force=True)
```

6.3.2 NOE script mode – initialisation of the data pipe

The start of this sample script is very similar to that of the relaxation curve-fitting calculation on page 55. The command

```
3 # Create the data pipe.
4 pipe.create('NOE', 'noe')
```

initialises the data pipe labelled “NOE”. The data pipe type is set to the NOE calculation by the argument “noe”.

6.3.3 NOE script mode – setting up the spin systems

The backbone amide nitrogen sequence is extracted from a PDB file using the same commands as the relaxation curve-fitting script (Chapter 5. The command

```
6 # Load the sequence from a PDB file.
7 structure.read_pdb('Ap4Aase_new_3.pdb')
```

will load the PDB file Ap4Aase_new_3.pdb into relax. Then the following commands will generate both the backbone amide and tryptophan indole ^{15}N spins

```
8 structure.load_spins(spin_id='@N')
9 structure.load_spins(spin_id='@NE1')
```

6.3.4 NOE script mode – loading the data

The commands

```
11 # Load the reference spectrum and saturated spectrum peak intensities.
12 spectrum.read_intensities(file='ref.list', spectrum_id='ref_ave')
13 spectrum.read_intensities(file='sat.list', spectrum_id='sat_ave')
```

will load the peak heights of the reference and saturated NOE experiments (although the volume could be used instead). relax will automatically determine the format of the peak list. Currently only Sparky, XEasy, NMRView and a generic columnar formatted text file are supported.

In this example, relax will determine from the file contents that these are Sparky peak lists (saved after typing “lt”). The first column of the file should be the Sparky assignment string and it is assumed that the 4th column contains either the peak height or peak volume (though this can be in any column – the `int_col` argument is used to specify where the data is). Without specifying the `int_method` argument, peak heights will be assumed. See page 378 for a description of all the `spectrum.read_intensities` user function arguments. In this example, the peak list looks like:

Assignment	w1	w2	Data	Height
LEU3N-HN	122.454	8.397	129722	
GLY4N-HN	111.999	8.719	422375	
SER5N-HN	115.085	8.176	384180	
MET6N-HN	120.934	8.812	272100	
ASP7N-HN	122.394	8.750	174970	
SER8N-HN	113.916	7.836	218762	
GLU11N-HN	122.194	8.604	30412	
GLY12N-HN	110.525	9.028	90144	

For subsequent usage of the data in relax, assuming a 3D structure exists, it is currently advisable to use the same residue and atom numbering as found in the PDB file.

If you have any other format you would like read by relax please send an email to the relax development mailing list detailing the software used, the format of the file (specifically where the residue number and peak intensity are located), and possibly attaching an example of the file itself.

6.3.5 NOE script mode – setting the errors

In this example the errors were measured from the base plain noise. The Sparky RMSD function was used to estimate the maximal noise levels across the spectrum in regions containing no peaks. For the reference spectrum the RMSD was approximately 3600 whereas in the saturated spectrum the RMSD was 3000. These errors are set by the commands

```
21 # Set the errors.
22 spectrum.baseplane_rmsd(error=3600, spectrum_id='ref_ave')
23 spectrum.baseplane_rmsd(error=3000, spectrum_id='sat_ave')
```

For the residue G114, the noise levels are significantly increased compared to the rest of the protein as the peak is located close to the water signal. The higher errors for this residue are specified by the commands

```
25 # Individual residue errors.
26 spectrum.baseplane_rmsd(error=122000, spectrum_type='ref', res_num=114)
27 spectrum.baseplane_rmsd(error=8500, spectrum_type='sat', res_num=114)
```

There are many other ways of setting the errors, for example via spectrum duplication, triplification, etc. See the documentation for the `spectrum.error_analysis` user function on page 376 for all possible options. This user function needs to be executed at this stage to correctly set up the errors for all spin systems:

```
29 # Peak intensity error analysis.
30 spectrum.error_analysis()
```

6.3.6 NOE script mode – unresolved spins

As the peaks of certain spins overlap to such an extent that the heights or volumes cannot be resolved, a simple text file was created called “unresolved” in which each line consists of the residue number followed by the atom name. By using the command

```

32 # Deselect unresolved spins.
33 deselect.read(name, file='unresolved', res_num_col=1, spin_name_col=2)

```

all spins in the file “unresolved” are excluded from the analysis.

6.3.7 NOE script mode – the NOE calculation

At this point the NOE can be calculated. The user function

```

35 # Calculate the NOEs.
36 calc()

```

will calculate both the NOE and the errors. The NOE value will be calculated using the formula

$$NOE = \frac{I_{sat}}{I_{ref}}, \quad (6.1)$$

where I_{sat} is the intensity of the peak in the saturated spectrum and I_{ref} is that of the reference spectrum. The error is calculated by

$$\sigma_{NOE} = \sqrt{\frac{(\sigma_{sat} \cdot I_{ref})^2 + (\sigma_{ref} \cdot I_{sat})^2}{I_{ref}}}, \quad (6.2)$$

where σ_{sat} and σ_{ref} are the peak intensity errors in the saturated and reference spectra respectively. To create a file of the NOEs the command

```

38 # Save the NOEs.
39 value.write(param='noe', file='noe.out', force=True)

```

will create a file called `noe.out` with the NOE values and errors. The force flag will cause any file with the same name to be overwritten. An example of the format of `noe.out` is

# mol_name	res_num	res_name	spin_num	spin_name	value	error
Ap4Aase_new_3_mol1	1	GLY	1	N	None	None
Ap4Aase_new_3_mol1	2	PRO	11	N	None	None
Ap4Aase_new_3_mol1	3	LEU	28	N	None	None
Ap4Aase_new_3_mol1	4	GLY	51	N	-0.038921946984531344	0.019031770246176943
Ap4Aase_new_3_mol1	5	SER	59	N	-0.312404225679127	0.018596937298386886
Ap4Aase_new_3_mol1	6	MET	71	N	-0.42850831873249773	0.02525856323041225
Ap4Aase_new_3_mol1	7	ASP	91	N	-0.5305492810313481	0.027990623144176396
Ap4Aase_new_3_mol1	8	SER	104	N	-0.5652842977581912	0.021706121467731133
Ap4Aase_new_3_mol1	9	PRO	116	N	None	None
Ap4Aase_new_3_mol1	10	PRO	133	N	None	None
Ap4Aase_new_3_mol1	11	GLU	150	N	None	None
Ap4Aase_new_3_mol1	12	GLY	167	N	-0.7036626368123614	0.04681370194503697
Ap4Aase_new_3_mol1	13	TYR	175	N	-0.747464566367261	0.03594640051809186
Ap4Aase_new_3_mol1	14	ARG	200	N	-0.7524129557634996	0.04957018638401278

6.3.8 NOE script mode – viewing the results

Any two dimensional data set can be plotted in relax in conjunction with the program `Grace`. The program is also known as `Xmgrace` and was previously known as `ACE/gr` or `Xmgr`. The highly flexible relax user function `grace.write` is capable of producing 2D plots of any x-y data sets. The three commands

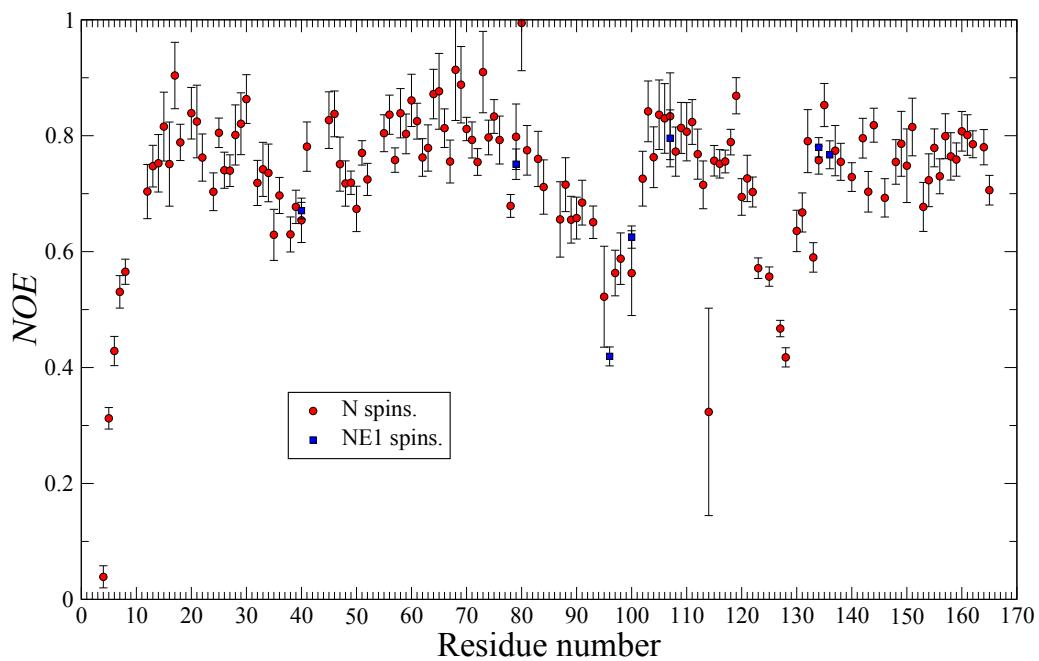


Figure 6.1: A Grace plot of the NOE value and error against the residue number. This is an example of the output of the user function `grace.write`.

```
41 # Create Grace files.
42 grace.write(y_data_type='ref', file='ref.agr', force=True)
43 grace.write(y_data_type='sat', file='sat.agr', force=True)
44 grace.write(y_data_type='noe', file='noe.agr', force=True)
```

will create three separate plots of the peak intensity of the reference and saturated spectra as well as the NOE. The x-axis in all three defaults to the residue number. As the x and y-axes can be any parameter the command

```
grace.write(x_data_type='ref', y_data_type='sat', file='ref_vs_sat.agr', force=True)
```

would create a plot of the reference verses the saturated intensity with one point per residue. Returning to the sample script three Grace data files are created `ref.agr`, `sat.agr` and `noe.agr` and placed in the default directory `./grace`. These can be visualised by opening the file within Grace. However relax will do that for you with the commands

```
46 # View the Grace files.
47 grace.view(file='ref.agr')
48 grace.view(file='sat.agr')
49 grace.view(file='noe.agr')
```

An example of the output after modifying the axes is shown in figure 6.1.

6.4 The NOE auto-analysis in the GUI

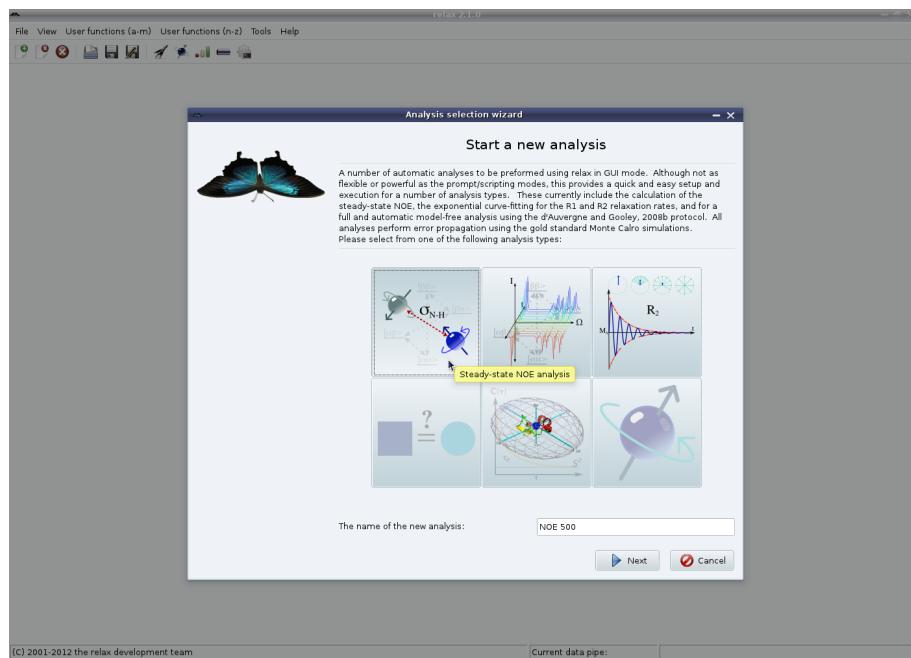
The relax graphical user interface provides access to an automated steady-state NOE analysis. This auto-analysis operates in the same way as the sample script described earlier in this chapter. In this example, relax will be launched with:

```
$ relax --log log --gui
```

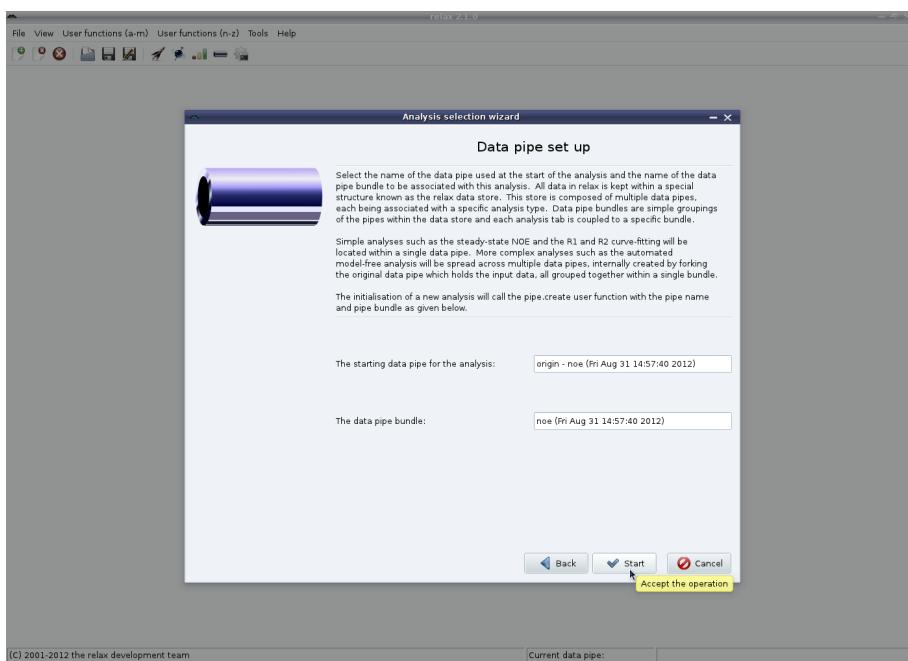
The `--log` command line argument will cause all of relax's text printouts to be placed into the `log` file which can serve as a record for later reference (the `--tee` command line argument could be used as well).

6.4.1 NOE GUI mode – initialisation of the data pipe

First launch the analysis selection wizard (see Figure 1.4 on page 12). Select the NOE analysis and, if you plan on running steady-state NOE analyses from multiple fields in one relax instance, change the name of the analysis:

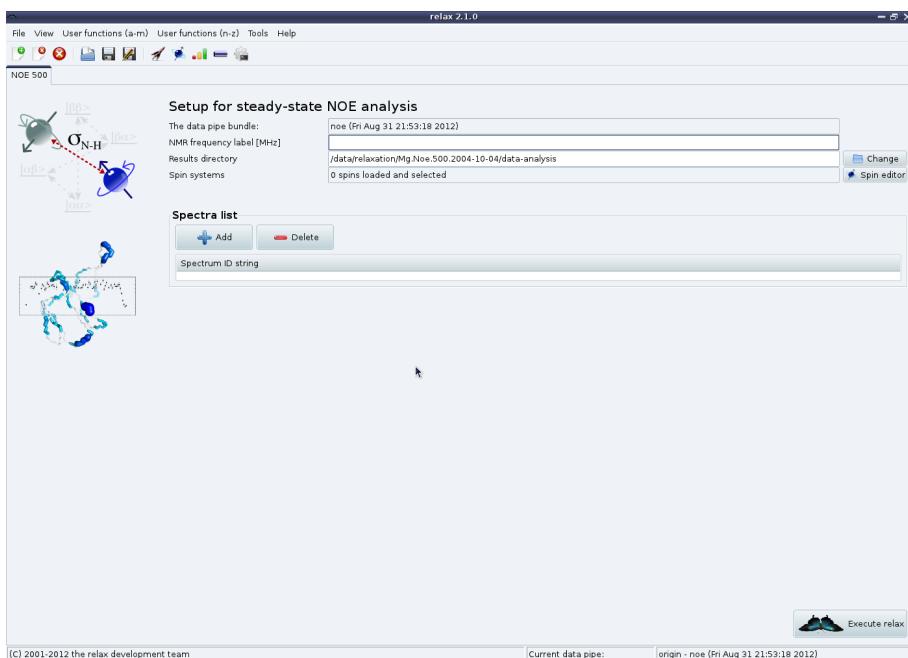


The second part of the wizard need not be modified, just click on “Start” to begin. This will create a dedicated data pipe for the analysis. A data pipe bundle will also be created, but for the steady-state NOE will only contain a single data throughout the analysis.



6.4.2 NOE GUI mode – general setup

You should then see the blank analysis tab:



The first thing to do now is to set the NMR frequency label. This is only used for the name of the NOE output file. For example if you set the label to “500”, the file `noe.500.out` will be created at the end of the analysis.

You can also choose to change the “Results directory” where all of the automatically created results files will be placed. These two steps are unique to the GUI mode.

6.4.3 NOE GUI mode – setting up the spin systems

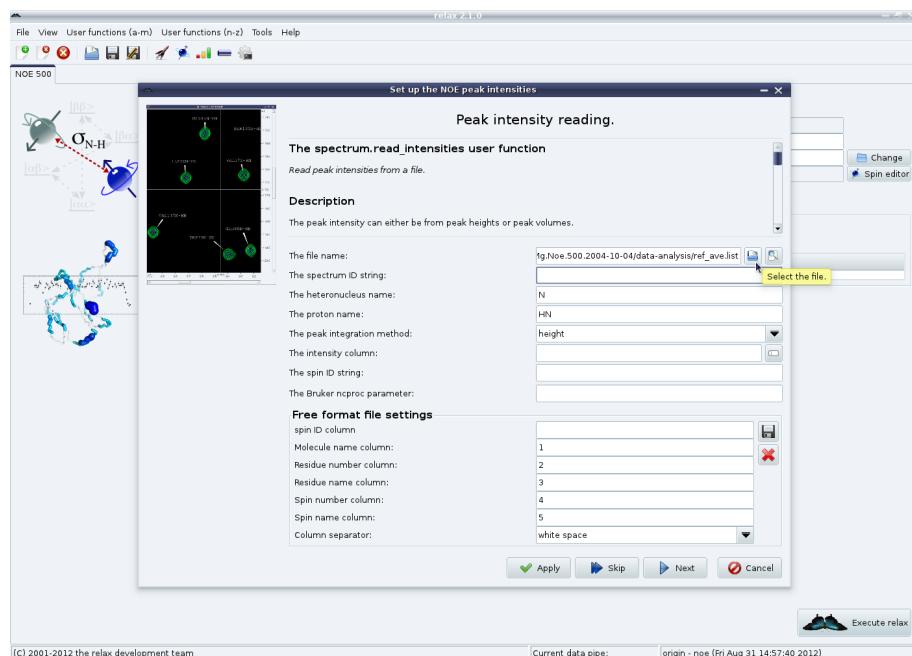
Just as in the prompt and scripting UI modes, the molecule, residue and spin data structures need to be set up prior to the loading of any spin specific data. The “Spin systems” GUI element is used for this purpose. Before any spin systems have been set up, this should say something like “0 spins loaded and selected”. To fix this, click on the “Spin editor” button and you should then see the spin viewer window. The next steps are fully described in section 4.5.2 on page 40 for PDB files or section 4.5.3 on page 43 for a sequence file. The spin viewer window can now be closed.

6.4.4 NOE GUI mode – unresolved spins

Using the unresolved spins file as described in the prompt/script UI sections, the same spins can be deselected at this point. See Section 4.5.5 on page 44 for the details of how to deselect the spins in the GUI.

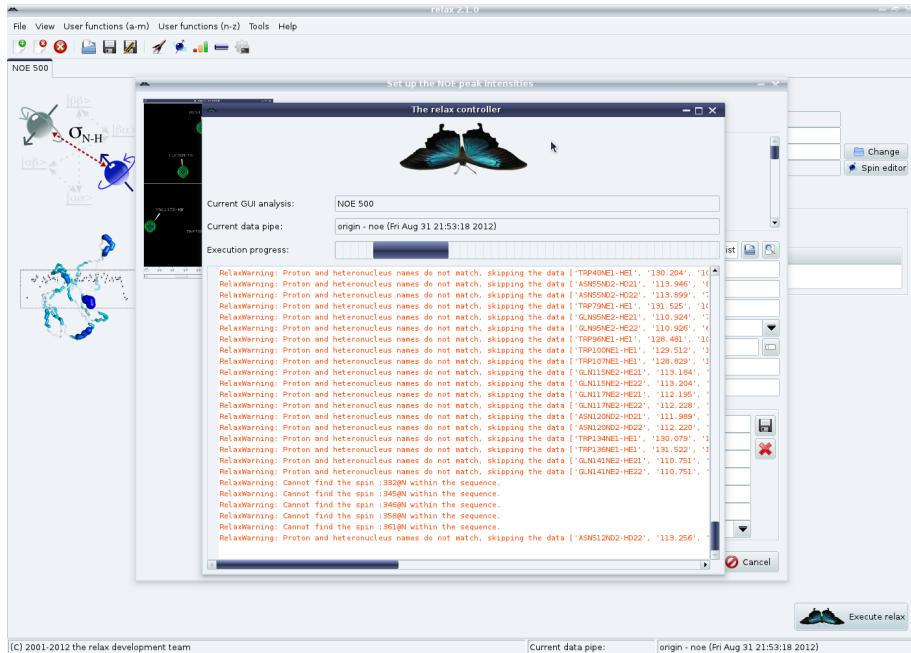
6.4.5 NOE GUI mode – loading the data

The next step is to load the saturated and reference NOE peak lists. From the main NOE auto-analysis tab, click on the “Add” button in the “Spectra list” GUI element. This will launch the NOE peak intensity loading wizard. From the first wizard page, select the peak list file containing the reference intensities (from the averaged shift list):

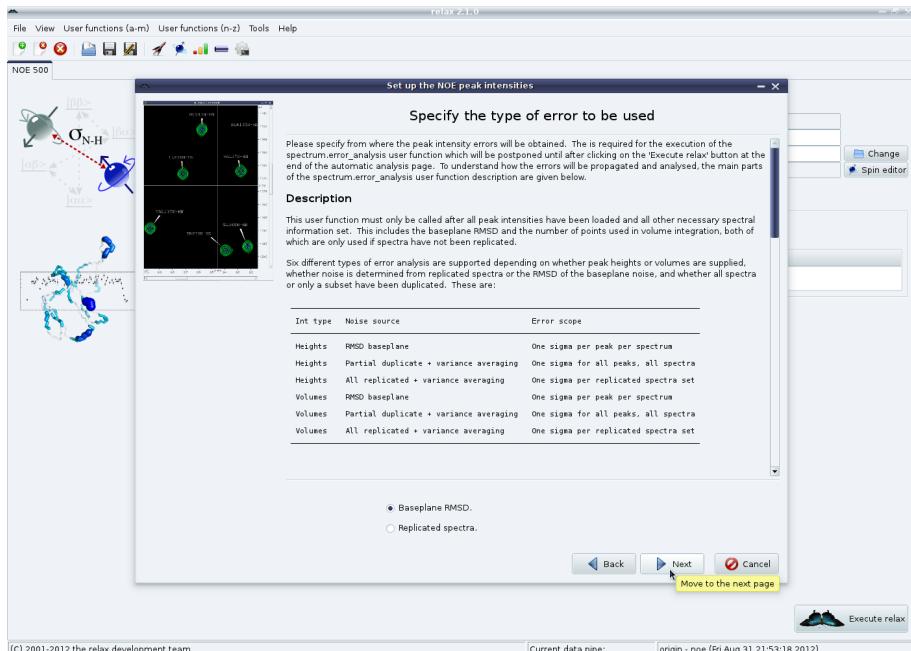


Then set the obligatory spectrum ID string to a unique value (in this case “ref”). The spectral dimension may need to be changed so that the peak intensities are associated with the correct atom of the pair. In case you have forgotten the spin names or the format of the peak list next to the file name selection button is a preview button which can be used to open the peak list in the default text editor. Set the other fields as needed. Click on “Next”. Note that a `RelaxWarning` will be thrown for all peak list entries which do

not match a spin system within the relax data store. This will cause the relax controller window to appear:

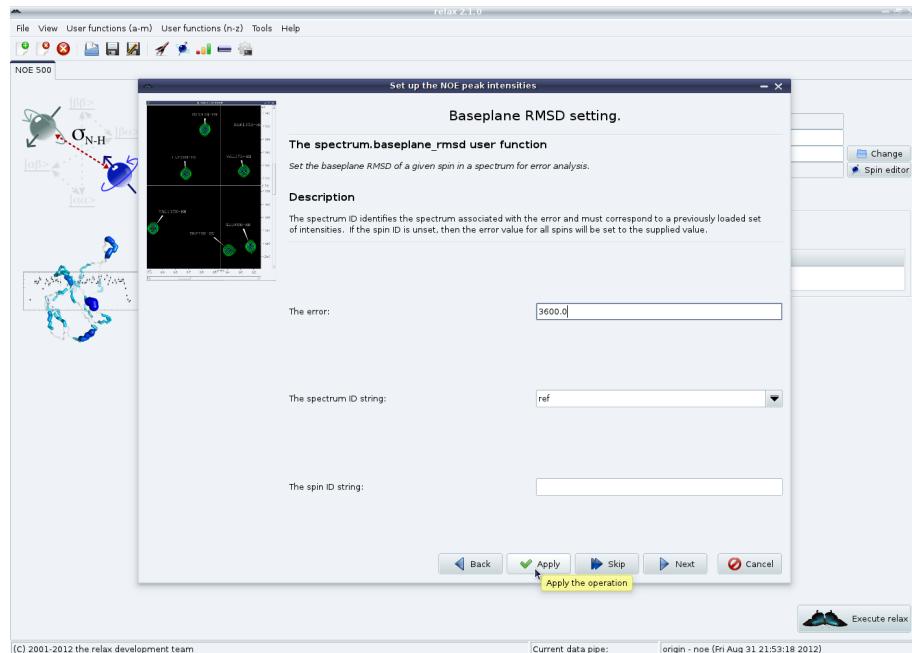


Carefully check these warnings to be sure that the data is correctly loaded and, if everything is fine, the relax controller window can be closed. If the dimension has been wrongly specified or some other setting is incorrect a **RelaxError** might appear saying that no data was loaded – you will then need to fix the settings and click on “Apply” again. The error type page should now appear.

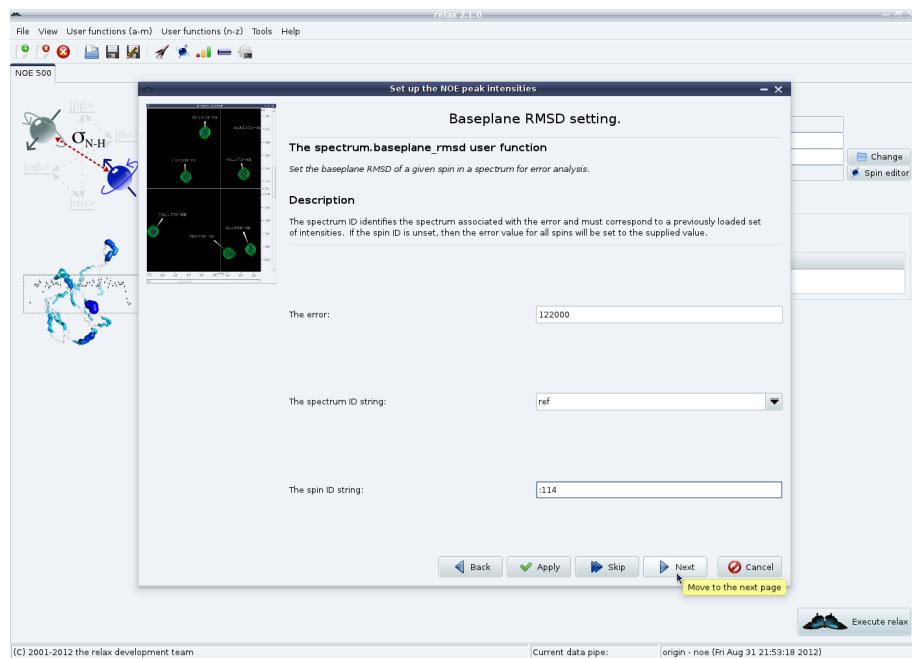


Please read the description in this window very carefully to know what to do next. In this example, we will choose “Baseplane RMSD”. For this specific example, Sparky’s “Extensions→Spectrum→Spectrum baseplane RMSD” option in the “F1” selection mode was used to measure empty regions of the spectrum (mainly in the random coil region) to

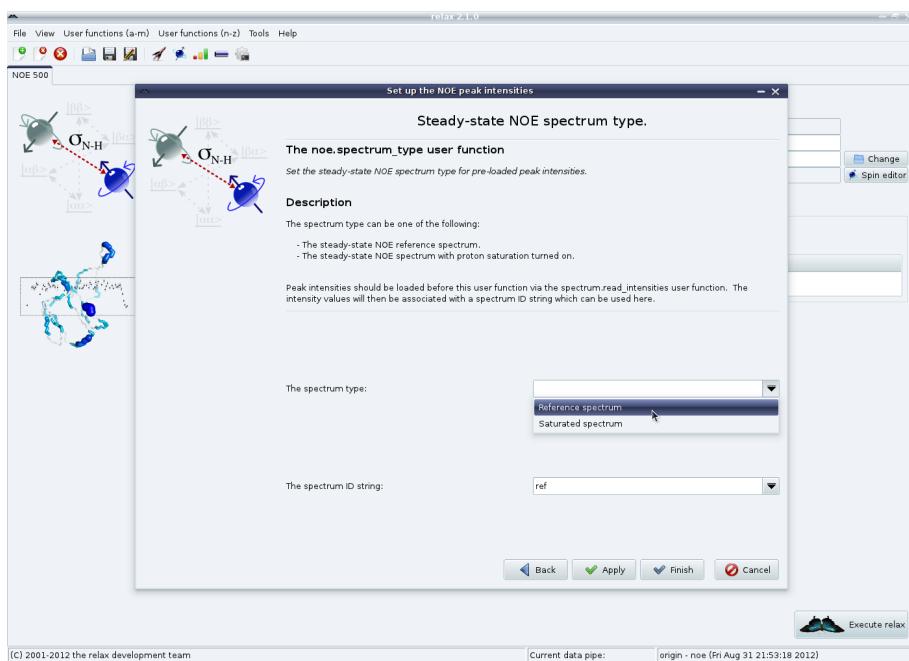
determine an average RMSD of approximately 3600. Set the value and click on “Apply”.



As glycine 114 is located close to the noise signal, its error was much higher at 122000. Individual spin errors can be set via the spin ID string (see section 4.2.2 on page 36 for information about spin IDs):

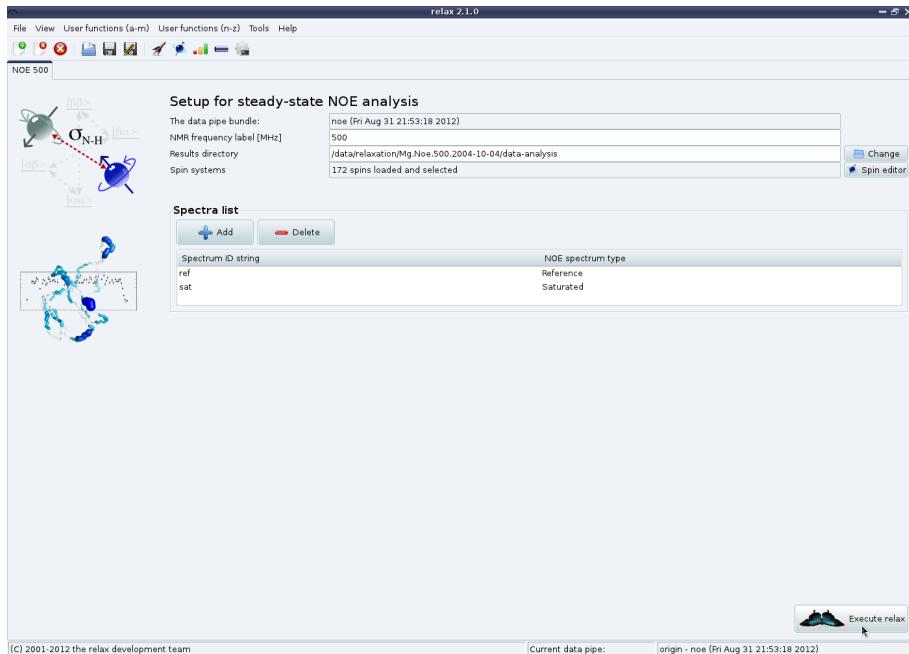


Finally select which type of spectrum this is and click on “Finish”:



The entire procedure should be repeated for the saturated spectrum (or you may have worked out that both can be loaded simultaneously by using the “Apply” button more often). For this example, the spectrum ID was set to “sat” and the baseplane RMSD to 3000 for all spins (except for G114 which had an error of 8500).

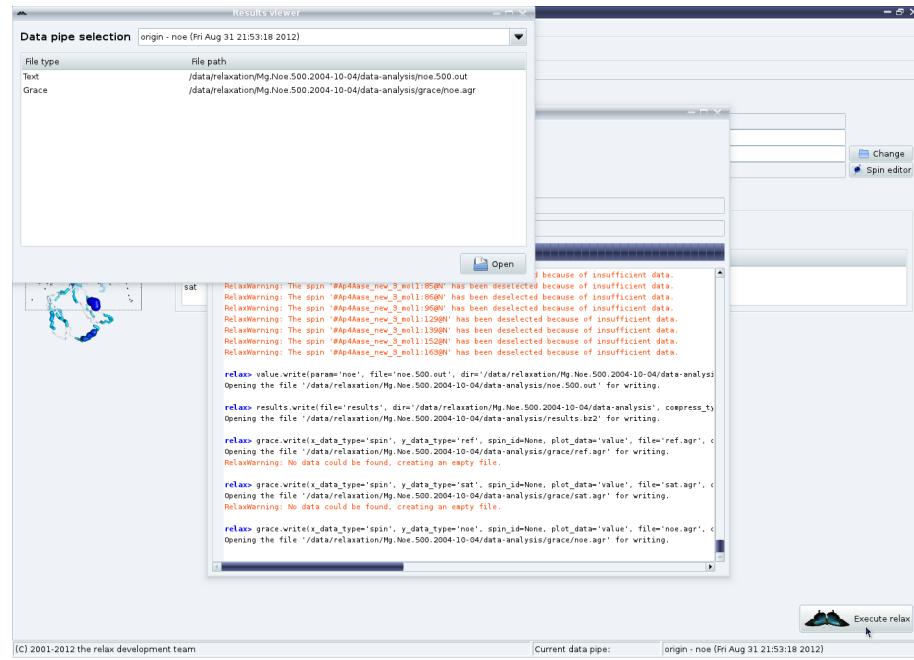
The NOE analysis tab should now look like:



6.4.6 NOE GUI mode – the NOE calculation

Now that everything is set up, simply click on “Execute relax” in the NOE analysis tab. The relax controller window will appear displaying many messages. These should all be

checked very carefully to make sure that everything has executed as you expected. The “Results viewer” window will also appear:

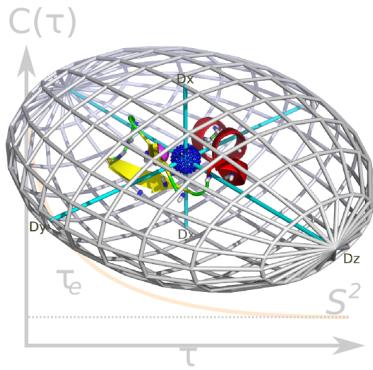


The results viewer window can be used to launch a text editor to see the NOE values and error or Grace to visualise the results (see Figure 6.1 on page 74).

As a last step, the relax state can be saved (via the “File” menu) and relax closed. Take one last look at the `noe.out` log file to be certain that there are no strange warnings or errors.

Chapter 7

Model-free analysis



7.1 Model-free theory

7.1.1 The chi-squared function – $\chi^2(\theta)$

The chi-squared equation is itself dependent on the relaxation equations through the back-calculated relaxation data $R(\theta)$. Letting the relaxation values of the set $R(\theta)$ be the $R_1(\theta)$, $R_2(\theta)$, and $\text{NOE}(\theta)$ an additional layer of abstraction can be used to simplify the calculation of the gradients and Hessians. This involves decomposing the NOE equation into the cross relaxation rate constant $\sigma_{\text{NOE}}(\theta)$ and the auto relaxation rate $R_1(\theta)$. Taking equation (7.5) below the transformed relaxation equations are

$$R_1(\theta) = R'_1(\theta), \quad (7.1a)$$

$$R_2(\theta) = R'_2(\theta), \quad (7.1b)$$

$$\text{NOE}(\theta) = 1 + \frac{\gamma_H}{\gamma_X} \frac{\sigma_{\text{NOE}}(\theta)}{R_1(\theta)}. \quad (7.1c)$$

whereas the relaxation equations are the $R_1(\theta)$, $R_2(\theta)$, $\sigma_{\text{NOE}}(\theta)$.

7.1.2 The relaxation equations – $R'_i(\theta)$

The relaxation values of the set $R'(\theta)$ include the spin-lattice, spin-spin, and cross-relaxation rates at all field strengths. These rates are respectively (Abragam, 1961)

$$R_1(\theta) = d \left(J(\omega_H - \omega_X) + 3J(\omega_X) + 6J(\omega_H + \omega_X) \right) + cJ(\omega_X), \quad (7.2a)$$

$$\begin{aligned} R_2(\theta) &= \frac{d}{2} \left(4J(0) + J(\omega_H - \omega_X) + 3J(\omega_X) + 6J(\omega_H) \right. \\ &\quad \left. + 6J(\omega_H + \omega_X) \right) + \frac{c}{6} \left(4J(0) + 3J(\omega_X) \right) + R_{ex}, \end{aligned} \quad (7.2b)$$

$$\sigma_{\text{NOE}}(\theta) = d \left(6J(\omega_H + \omega_X) - J(\omega_H - \omega_X) \right), \quad (7.2c)$$

where $J(\omega)$ is the power spectral density function and R_{ex} is the relaxation due to chemical exchange. The dipolar and CSA constants are defined in SI units as

$$d = \frac{1}{4} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{(\gamma_H \gamma_X \hbar)^2}{\langle r^6 \rangle}, \quad (7.3)$$

$$c = \frac{(\omega_H \Delta\sigma)^2}{3}, \quad (7.4)$$

where μ_0 is the permeability of free space, γ_H and γ_X are the gyromagnetic ratios of the H and X spins respectively, \hbar is Plank's constant divided by 2π , r is the bond length, and $\Delta\sigma$ is the chemical shift anisotropy measured in ppm. The cross-relaxation rate σ_{NOE} is related to the steady state NOE by the equation

$$\text{NOE}(\theta) = 1 + \frac{\gamma_H}{\gamma_X} \frac{\sigma_{\text{NOE}}(\theta)}{R_1(\theta)}. \quad (7.5)$$

7.1.3 The spectral density functions – $J(\omega)$

The relaxation equations are themselves dependent on the calculation of the spectral density values $J(\omega)$. Within model-free analysis these are modelled by the original model-free formula (Lipari and Szabo, 1982a,b)

$$J(\omega) = \frac{2}{5} \sum_{i=-k}^k c_i \cdot \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right), \quad (7.6)$$

where S^2 is the square of the Lipari and Szabo generalised order parameter and τ_e is the effective correlation time. The order parameter reflects the amplitude of the motion and the correlation time in an indication of the time scale of that motion. The theory was extended by Clore et al. (1990) by the modelling of two independent internal motions using the equation

$$\begin{aligned} J(\omega) &= \frac{2}{5} \sum_{i=-k}^k c_i \cdot \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} \right. \\ &\quad \left. + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (7.7) \end{aligned}$$

where S_f^2 and τ_f are the amplitude and timescale of the faster of the two motions whereas S_s^2 and τ_s are those of the slower motion. S_f^2 and S_s^2 are related by the formula $S^2 = S_f^2 \cdot S_s^2$.

If these forms of the model-free spectral density functions are unfamiliar, that is because these are the numerically stabilised forms presented in [d'Auvergne and Gooley \(2008a\)](#). The original model-free spectral density functions presented in [Lipari and Szabo \(1982a\)](#) and [Clore et al. \(1990\)](#) are not the most numerically stable form of these equations. An important problem encountered in optimisation is round-off error in which machine precision influences the result of mathematical operations. The double reciprocal $\tau^{-1} = \tau_m^{-1} + \tau_e^{-1}$ used in the equations are operations which are particularly susceptible to round-off error, especially when $\tau_e \ll \tau_m$. By incorporating these reciprocals into the model-free spectral density functions and then simplifying the equations this source of round-off error can be eliminated, giving relax an edge over other model-free optimisation software.

7.1.4 Brownian rotational diffusion

In equations (7.6) and (7.7) the generic Brownian diffusion NMR correlation function presented in [d'Auvergne \(2006\)](#) has been used. This function is

$$C(\tau) = \frac{1}{5} \sum_{i=-k}^k c_i \cdot e^{-\tau/\tau_i}, \quad (7.8)$$

where the summation index i ranges over the number of exponential terms within the correlation function. This equation is generic in that it can describe the diffusion of an ellipsoid, a spheroid, or a sphere.

Diffusion as an ellipsoid

For the ellipsoid defined by the parameter set $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$ the variable k is equal to two and therefore the index $i \in \{-2, -1, 0, 1, 2\}$. The geometric parameters $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r\}$ are defined as

$$\mathfrak{D}_{iso} = \frac{1}{3}(\mathfrak{D}_x + \mathfrak{D}_y + \mathfrak{D}_z), \quad (7.9a)$$

$$\mathfrak{D}_a = \mathfrak{D}_z - \frac{1}{2}(\mathfrak{D}_x + \mathfrak{D}_y), \quad (7.9b)$$

$$\mathfrak{D}_r = \frac{\mathfrak{D}_y - \mathfrak{D}_x}{2\mathfrak{D}_a}, \quad (7.9c)$$

and are constrained by

$$0 < \mathfrak{D}_{iso} < \infty, \quad (7.10a)$$

$$0 \leq \mathfrak{D}_a < \frac{\mathfrak{D}_{iso}}{\frac{1}{3} + \mathfrak{D}_r} \leq 3\mathfrak{D}_{iso}, \quad (7.10b)$$

$$0 \leq \mathfrak{D}_r \leq 1. \quad (7.10c)$$

The orientational parameters $\{\alpha, \beta, \gamma\}$ are the Euler angles using the z-y-z rotation notation.

The five weights c_i are defined as

$$c_{-2} = \frac{1}{4}(d - e), \quad (7.11a)$$

$$c_{-1} = 3\delta_y^2\delta_z^2, \quad (7.11b)$$

$$c_0 = 3\delta_x^2\delta_z^2, \quad (7.11c)$$

$$c_1 = 3\delta_x^2\delta_y^2, \quad (7.11d)$$

$$c_2 = \frac{1}{4}(d + e), \quad (7.11e)$$

where

$$d = 3(\delta_x^4 + \delta_y^4 + \delta_z^4) - 1, \quad (7.12)$$

$$e = \frac{1}{\mathfrak{R}} \left[(1 + 3\mathfrak{D}_r)(\delta_x^4 + 2\delta_y^2\delta_z^2) + (1 - 3\mathfrak{D}_r)(\delta_y^4 + 2\delta_x^2\delta_z^2) - 2(\delta_z^4 + 2\delta_x^2\delta_y^2) \right], \quad (7.13)$$

and where

$$\mathfrak{R} = \sqrt{1 + 3\mathfrak{D}_r^2}. \quad (7.14)$$

The five correlation times τ_i are

$$1/\tau_{-2} = 6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R}, \quad (7.15a)$$

$$1/\tau_{-1} = 6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r), \quad (7.15b)$$

$$1/\tau_0 = 6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r), \quad (7.15c)$$

$$1/\tau_1 = 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a, \quad (7.15d)$$

$$1/\tau_2 = 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R}. \quad (7.15e)$$

Diffusion as a spheroid

The variable k is equal to one in the case of the spheroid defined by the parameter set $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \theta, \phi\}$, hence $i \in \{-1, 0, 1\}$. The geometric parameters $\{\mathfrak{D}_{iso}, \mathfrak{D}_a\}$ are defined as

$$\mathfrak{D}_{iso} = \frac{1}{3}(\mathfrak{D}_{\parallel} + 2\mathfrak{D}_{\perp}), \quad (7.16a)$$

$$\mathfrak{D}_a = \mathfrak{D}_{\parallel} - \mathfrak{D}_{\perp}. \quad (7.16b)$$

and are constrained by

$$0 < \mathfrak{D}_{iso} < \infty, \quad (7.17a)$$

$$-\frac{3}{2}\mathfrak{D}_{iso} < \mathfrak{D}_a < 3\mathfrak{D}_{iso}. \quad (7.17b)$$

The orientational parameters $\{\theta, \phi\}$ are the spherical angles defining the orientation of the major axis of the diffusion frame within the lab frame.

The three weights c_i are

$$c_{-1} = \frac{1}{4}(3\delta_z^2 - 1)^2, \quad (7.18a)$$

$$c_0 = 3\delta_z^2(1 - \delta_z^2), \quad (7.18b)$$

$$c_1 = \frac{3}{4}(\delta_z^2 - 1)^2. \quad (7.18c)$$

The five correlation times τ_i are

$$1/\tau_{-1} = 6\mathfrak{D}_{iso} - 2\mathfrak{D}_a, \quad (7.19a)$$

$$1/\tau_0 = 6\mathfrak{D}_{iso} - \mathfrak{D}_a, \quad (7.19b)$$

$$1/\tau_1 = 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a. \quad (7.19c)$$

Diffusion as a sphere

In the situation of a molecule diffusing as a sphere either described by the single parameter τ_m or \mathfrak{D}_{iso} , the variable k is equal to zero. Therefore $i \in \{0\}$. The single weight c_0 is equal to one and the single correlation time τ_0 is equivalent to the global tumbling time τ_m given by

$$1/\tau_m = 6\mathfrak{D}_{iso}. \quad (7.20)$$

This is diffusion equation presented in [Bloembergen et al. \(1948\)](#).

7.1.5 The model-free models

Extending the list of models given in [Mandel et al. \(1995\)](#); [Fushman et al. \(1997\)](#); [Orekhov et al. \(1999a\)](#); [Korzhnev et al. \(2001\)](#); [Zhuravleva et al. \(2004\)](#), the models built into relax include

$$m0 = \{\}, \quad (7.21.0)$$

$$m1 = \{S^2\}, \quad (7.21.1)$$

$$m2 = \{S^2, \tau_e\}, \quad (7.21.2)$$

$$m3 = \{S^2, R_{ex}\}, \quad (7.21.3)$$

$$m4 = \{S^2, \tau_e, R_{ex}\}, \quad (7.21.4)$$

$$m5 = \{S^2, S_f^2, \tau_s\}, \quad (7.21.5)$$

$$m6 = \{S^2, \tau_f, S_f^2, \tau_s\}, \quad (7.21.6)$$

$$m7 = \{S^2, S_f^2, \tau_s, R_{ex}\}, \quad (7.21.7)$$

$$m8 = \{S^2, \tau_f, S_f^2, \tau_s, R_{ex}\}, \quad (7.21.8)$$

$$m9 = \{R_{ex}\}. \quad (7.21.9)$$

The parameter R_{ex} is scaled quadratically with field strength in these models as it is assumed to be fast. In the set theory notation, the model-free model for the spin system i is represented by the symbol \mathfrak{F}_i . Through the addition of the local τ_m to each of these models, only the component of Brownian rotational diffusion experienced by the spin

system is probed. These models, represented in set notation by the symbol \mathfrak{T}_i , are

$$tm0 = \{\tau_m\}, \quad (7.22.0)$$

$$tm1 = \{\tau_m, S^2\}, \quad (7.22.1)$$

$$tm2 = \{\tau_m, S^2, \tau_e\}, \quad (7.22.2)$$

$$tm3 = \{\tau_m, S^2, R_{ex}\}, \quad (7.22.3)$$

$$tm4 = \{\tau_m, S^2, \tau_e, R_{ex}\}, \quad (7.22.4)$$

$$tm5 = \{\tau_m, S^2, S_f^2, \tau_s\}, \quad (7.22.5)$$

$$tm6 = \{\tau_m, S^2, \tau_f, S_f^2, \tau_s\}, \quad (7.22.6)$$

$$tm7 = \{\tau_m, S^2, S_f^2, \tau_s, R_{ex}\}, \quad (7.22.7)$$

$$tm8 = \{\tau_m, S^2, \tau_f, S_f^2, \tau_s, R_{ex}\}, \quad (7.22.8)$$

$$tm9 = \{\tau_m, R_{ex}\}. \quad (7.22.9)$$

7.1.6 Model-free optimisation theory

The implementation of optimisation in relax is discussed in detail in Chapter 11. To understand the concepts in this subsection, it is best to look at that chapter first.

The model-free space

In model-free analysis the target function $f(\theta)$ is the chi-squared equation

$$\chi^2(\theta) = \sum_{i=1}^n \frac{(R_i - R_i(\theta))^2}{\sigma_i^2}, \quad (7.23)$$

where i is the summation index, R_i is the experimental relaxation data which belongs to the data set R and includes the R_1 , R_2 , and NOE values at all field strengths, $R_i(\theta)$ is the back calculated relaxation data belonging to the set $R(\theta)$, and σ_i is the experimental error. For the optimisation of the model-free parameters while the diffusion tensor is held fixed, the summation index ranges over the relaxation data of an individual spin. If the diffusion parameters are optimised simultaneously with the model-free parameters the summation index ranges over all relaxation data of all selected spins of the macromolecule.

Given the current parameter values the model-free function provided to the algorithm will calculate the value of the model-free spectral density function $J(\omega)$ at the five frequencies which induce NMR relaxation by using Equations (7.6) and (7.7). The theoretical R_1 , R_2 , and NOE values are then back-calculated using Equations (7.2a), (7.2b), (7.2c), and (7.5). Finally, the chi-squared value is calculated using Equation (7.23).

To produce the gradient and Hessian required for model-free optimisation a large chain of first and second partial derivatives needs to be calculated. Firstly the partial derivatives of the spectral density functions (7.6) and (7.7) are necessary. Then the partial derivatives of the relaxation equations (7.2a) to (7.2c) followed by the NOE equation (7.5) are needed. Finally the partial derivative of the chi-squared formula (7.23) is required. These first and second partial derivatives, as well as those of the components of the Brownian diffusion correlation function for non-isotropic tumbling, are presented as Chapter 12.

Grid search

Due to the complexity of the curvature of the model-free space, the grid point with the lowest chi-squared value may in fact be on the opposite side of the space to the local minimum. Therefore the model-free space renders many optimisation algorithms ineffective (d'Auvergne and Gooley, 2008a).

Parameter constraints

To understand this section, please see Section 11.5 on page 172. For model-free analysis, linear constraints are the most useful type of constraint as the correlation time τ_f can be restricted to being less than τ_s by using the inequality $\tau_s - \tau_f \geq 0$.

For the parameters specific to individual spins the linear constraints in the notation of (11.18) are

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} S^2 \\ S_f^2 \\ S_s^2 \\ \tau_e \\ \tau_f \\ \tau_s \\ R_{ex} \\ r \\ CSA \end{pmatrix} \geq \begin{pmatrix} 0 \\ -1 \\ 0 \\ -1 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0.9e^{-10} \\ 2e^{-10} \\ 300e^{-6} \\ 0 \end{pmatrix}. \quad (7.24)$$

Through the isolation of each individual element, the constraints can be seen to be equivalent to

$$0 \leq S^2 \leq 1, \quad (7.25a)$$

$$0 \leq S_f^2 \leq 1, \quad (7.25b)$$

$$0 \leq S_s^2 \leq 1, \quad (7.25c)$$

$$S^2 \leq S_f^2, \quad (7.25d)$$

$$S^2 \leq S_s^2, \quad (7.25e)$$

$$\tau_e \geq 0, \quad (7.25f)$$

$$\tau_f \geq 0, \quad (7.25g)$$

$$\tau_s \geq 0, \quad (7.25h)$$

$$\tau_s \geq 0, \quad (7.25i)$$

$$\tau_f \leq \tau_s, \quad (7.25j)$$

$$R_{ex} \geq 0, \quad (7.25k)$$

$$0.9e^{-10} \leq r \leq 2e^{-10}, \quad (7.25l)$$

$$-300e^{-6} \leq CSA \leq 0. \quad (7.25m)$$

To prevent the computationally expensive optimisation of failed models in which the internal correlation times minimise to infinity ([d'Auvergne and Gooley, 2006](#)), the constraint $\tau_e, \tau_f, \tau_s \leq 2\tau_m$ was implemented. When the global correlation time is fixed the constraints in the matrix notation of (11.18) are

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} \tau_e \\ \tau_f \\ \tau_s \end{pmatrix} \geq \begin{pmatrix} -2\tau_m \\ -2\tau_m \\ -2\tau_m \end{pmatrix}. \quad (7.26)$$

However when the global correlation time τ_m is one of the parameters being optimised the constraints become

$$\begin{pmatrix} 2 & -1 & 0 & 0 \\ 2 & 0 & -1 & 0 \\ 2 & 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} \tau_m \\ \tau_e \\ \tau_f \\ \tau_s \end{pmatrix} \geq \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \quad (7.27)$$

For the parameters of the diffusion tensor the constraints utilised are

$$0 \leq \tau_m \leq 200.0e^{-9}, \quad (7.28a)$$

$$\mathfrak{D}_a \geq 0, \quad (7.28b)$$

$$0 \leq \mathfrak{D}_r \leq 1, \quad (7.28c)$$

which in the matrix notation of (11.18) become

$$\begin{pmatrix} 1 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} \tau_m \\ \mathfrak{D}_a \\ \mathfrak{D}_r \end{pmatrix} \geq \begin{pmatrix} 0 \\ -200.0e^{-9} \\ 0 \\ 0 \\ -1 \end{pmatrix}. \quad (7.29)$$

The upper limit of 200 ns on τ_m prevents the parameter from heading towards infinity when model failure occurs ([d'Auvergne and Gooley \(2006\)](#)). This can significantly decrease the computation time. To isolate the prolate spheroid the constraint

$$(1) \cdot (\mathfrak{D}_a) \geq (0), \quad (7.30)$$

is used whereas to isolate the oblate spheroid the constraint used is

$$(-1) \cdot (\mathfrak{D}_a) \geq (0). \quad (7.31)$$

Dependent on the model optimised, the matrix A and vector b are constructed from combinations of the above linear constraints.

Diagonal scaling

The concept of diagonal scaling is explained in Section 11.6 on page 174.

For the model-free analysis the scaling factor of one is used for the order parameter and a scaling factor of $1e^{-12}$ is used for the correlation times. The R_{ex} parameter is scaled to be the chemical exchange rate of the first field strength. The scaling matrix for the parameters $\{S^2, S_f^2, S_s^2, \tau_e, \tau_f, \tau_s, R_{ex}, r, CSA\}$ of individual spins is

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1e^{-12} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1e^{-12} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1e^{-12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & (2\pi\omega_H)^{-2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1e^{-10} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1e^{-4} \end{pmatrix}. \quad (7.32)$$

For the ellipsoidal diffusion parameters $\{\tau_m, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$ the scaling matrix is

$$\begin{pmatrix} 1e^{-12} & 0 & 0 & 0 & 0 & 0 \\ 0 & 1e^7 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}. \quad (7.33)$$

For the spheroidal diffusion parameters $\{\tau_m, \mathfrak{D}_a, \theta, \phi\}$ the scaling matrix is

$$\begin{pmatrix} 1e^{-12} & 0 & 0 & 0 \\ 0 & 1e^7 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (7.34)$$

7.2 Optimisation of a single model-free model

7.2.1 Single model-free model script mode – the sample script

The sample script which demonstrates the optimisation of model-free model *m4* which consists of the parameters $\{S^2, \tau_e, R_{ex}\}$ is `model_free/single_model.py`. The text of the script is:

```

1 # Script for model-free analysis.
2
3 # Create the data pipe.
4 name = 'm4'
5 pipe.create(name, 'mf')
6
```

```

7 # Set up the 15N spins.
8 sequence.read('noe.500.out', res_num_col=1, res_name_col=2)
9 spin.name('N')
10 spin.element(element='N', spin_id='@N')
11 spin.isotope('15N', spin_id='@N')
12
13 # Load the relaxation data.
14 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
15   res_num_col=1, data_col=3, error_col=4)
16 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
17   res_num_col=1, data_col=3, error_col=4)
18 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
19   res_num_col=1, data_col=3, error_col=4)
20 relax_data.read(ri_id='R1_500', ri_type='R1', frq=500.0*1e6, file='r1.500.out',
21   res_num_col=1, data_col=3, error_col=4)
22 relax_data.read(ri_id='R2_500', ri_type='R2', frq=500.0*1e6, file='r2.500.out',
23   res_num_col=1, data_col=3, error_col=4)
24 relax_data.read(ri_id='NOE_500', ri_type='NOE', frq=500.0*1e6, file='noe.500.out',
25   res_num_col=1, data_col=3, error_col=4)
26
27 # Initialise the diffusion tensor.
28 diffusion_tensor.init(10e-9, fixed=True)
29
30 # Create all attached protons.
31 sequence.attach_protons()
32
33 # Define the magnetic dipole-dipole relaxation interaction.
34 interatom.define(spinid1='@N', spin_id2='@H', direct_bond=True)
35 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)
36 #interatom.unit_vectors()
37
38 # Define the CSA relaxation interaction.
39 value.set(-172 * 1e-6, 'csa')
40
41 # Select the model-free model.
42 model_free.select_model(model=name)
43
44 # Grid search.
45 grid_search(inc=11)
46
47 # Minimise.
48 minimise('newton')
49
50 # Monte Carlo simulations.
51 monte_carlo.setup(number=100)
52 monte_carlo.create_data()
53 monte_carlo.initial_values()
54 minimise('newton')
55 eliminate()
56 monte_carlo.error_analysis()
57
58 # Finish.
59 results.write(file='results', force=True)
60 state.save('save', force=True)

```

7.2.2 Single model-free model script mode – explanation

The above script consists of three major sections:

Loading of data Firstly a data pipe called “m4” is created to hold all of the analysis data.

Then the ^{15}N spin system data consisting of molecule, residue, and spin information is loaded into relax from the columns of the `noe.500.out` file, assuming that only residue numbers and names are present and are in the first and second columns respectively. The options of this `sequence.read` user function allow the molecule name, residue number, residue name, spin number, or spin name columns to be specified if desired. The ^{15}N spin is then set up using the `spin` user functions. The next part is to load all of the relaxation data, to set up the initial diffusion tensor, create the ^1H spins required for the magnetic dipole-dipole interaction, and to set up the magnetic dipole-dipole and CSA relaxation mechanisms. Finally the model-free model “m4” is chosen.

Optimisation The optimisation of model-free models requires an initial grid search to find a position close to the minimum, followed by the high precision Newton optimisation together with the Method of Multipliers constraint algorithm ([d'Auvergne and Gooley, 2008a](#)). Errors are propagated from the relaxation data to the model-free parameters via Monte Carlo simulations which is a multi-step process in relax (designed for flexibility and to teach how the simulations are constructed and carried out).

Data output The last stage consists of writing out the XML formatted results file which contains all of the data in the current data pipe, as well as the XML formatted save file which contains not only the current data pipe data but all of the relax data store data. Both files can be loaded back into relax later on.

7.3 Optimisation of all model-free models

7.3.1 All model-free models script mode – the sample script

The sample script which demonstrates the optimisation of all model-free models from $m0$ to $m9$ of individual spins is `model_free/mf_multimodel.py`. The important parts of the script are:

```

1 # Set the data pipe names (also the names of preset model-free models).
2 pipes = ['m0', 'm1', 'm2', 'm3', 'm4', 'm5', 'm6', 'm7', 'm8', 'm9']
3
4 # Loop over the pipes.
5 for name in pipes:
6     # Create the data pipe.
7     pipe.create(name, 'mf')
8
9     # Set up the  $^{15}\text{N}$  spins.
10    sequence.read('noe.500.out', res_num_col=1)
11    spin.name('N')
12    spin.element(element='N', spin_id='@N')
13    spin.isotope('15N', spin_id='@N')
14
15    # Load a PDB file.
16    structure.read_pdb('example.pdb')
17
18    # Load the relaxation data.
19    relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
res_num_col=1, data_col=3, error_col=4)
```

```

20   relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
21   res_num_col=1, data_col=3, error_col=4)
22   relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
23   res_num_col=1, data_col=3, error_col=4)
24   relax_data.read(ri_id='R1_500', ri_type='R1', frq=500.0*1e6, file='r1.500.out',
25   res_num_col=1, data_col=3, error_col=4)
26   relax_data.read(ri_id='R2_500', ri_type='R2', frq=500.0*1e6, file='r2.500.out',
27   res_num_col=1, data_col=3, error_col=4)
28   relax_data.read(ri_id='NOE_500', ri_type='NOE', frq=500.0*1e6, file='noe.500.out',
29   res_num_col=1, data_col=3, error_col=4)
30
31   # Set up the diffusion tensor.
32   diffusion_tensor.init(1e-8, fixed=True)
33
34   # Generate the 1H spins for the magnetic dipole-dipole relaxation interaction.
35   sequence.attach_protons()
36
37   # Define the magnetic dipole-dipole relaxation interaction.
38   interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
39   interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)
40   structure.get_pos('@N')
41   structure.get_pos('@H')
42   interatom.unit_vectors()
43
44   # Define the chemical shift relaxation interaction.
45   value.set(-172 * 1e-6, 'csa', spin_id='@N')
46
47   # Select the model-free model.
48   model_free.select_model(model=name)
49
50   # Minimise.
51   grid_search(inc=11)
52   minimise('newton')
53
54   # Write the results.
55   results.write(file='results', force=True)
56
57   # Save the program state.
58   state.save('save', force=True)

```

7.3.2 All model-free models script mode – explanation

The above script is very similar in spirit to the previous single model script in section 7.2 on page 91. The major difference is that this script loops over all of the model-free models, saving all of the results in the `save.bz2` file.

7.4 Model-free model selection

7.4.1 Model-free model selection script mode – the sample script

The sample script which demonstrates both model-free model elimination and model-free model selection between models from $m0$ to $m9$ is `model_free/modsel.py`. The text of the script is:

```

1 # Set the data pipe names.
2 pipes = ['m0', 'm1', 'm2', 'm3', 'm4', 'm5', 'm6', 'm7', 'm8', 'm9']
3
4 # Loop over the data pipe names.
5 for name in pipes:
6     print("\n\n# " + name + " #")
7
8     # Create the data pipe.
9     pipe.create(name, 'mf')
10
11    # Reload precalculated results from the file 'm1/results', etc.
12    results.read(file='results', dir=name)
13
14    # Model elimination.
15    eliminate()
16
17    # Model selection.
18    model_selection(method='AIC', modsel_pipe='aic')
19
20    # Write the results.
21    state.save('save', force=True)
22    results.write(file='results', force=True)

```

7.4.2 Model-free model selection script mode – explanation

This script is designed to be used in conjunction with the `model_free/mf_multimodel.py` script in the previous section. It will load all of the results files from the previous script and then perform the following:

Model-free model elimination The optimisation of model-free models performed by the previous script will fail for certain data sets together with certain models. To ensure that these models are never selected, they are removed from the analysis (see [d'Auvergne and Gooley \(2006\)](#)).

Model-free model selection The AIC model selection as described in [d'Auvergne and Gooley \(2003\)](#) will be used to determine which model-free model best describes the relaxation data.

Data output Finally both a save state and result file will be created.

These three sample scripts describe the basic components of model-free analysis. However a full analysis requires the construction of a much more complex iterative procedure. The following sections will describe both the original diffusion seeded approaches as well as the new model-free protocol built into relax.

7.5 The methodology of Mandel et al., 1995

By presenting a systematic methodology for obtaining a consistent model-free description of the dynamics of the system, the manuscript of [Mandel et al. \(1995\)](#) revolutionised the application of model-free analysis. The full protocol is presented in Figure 7.1.

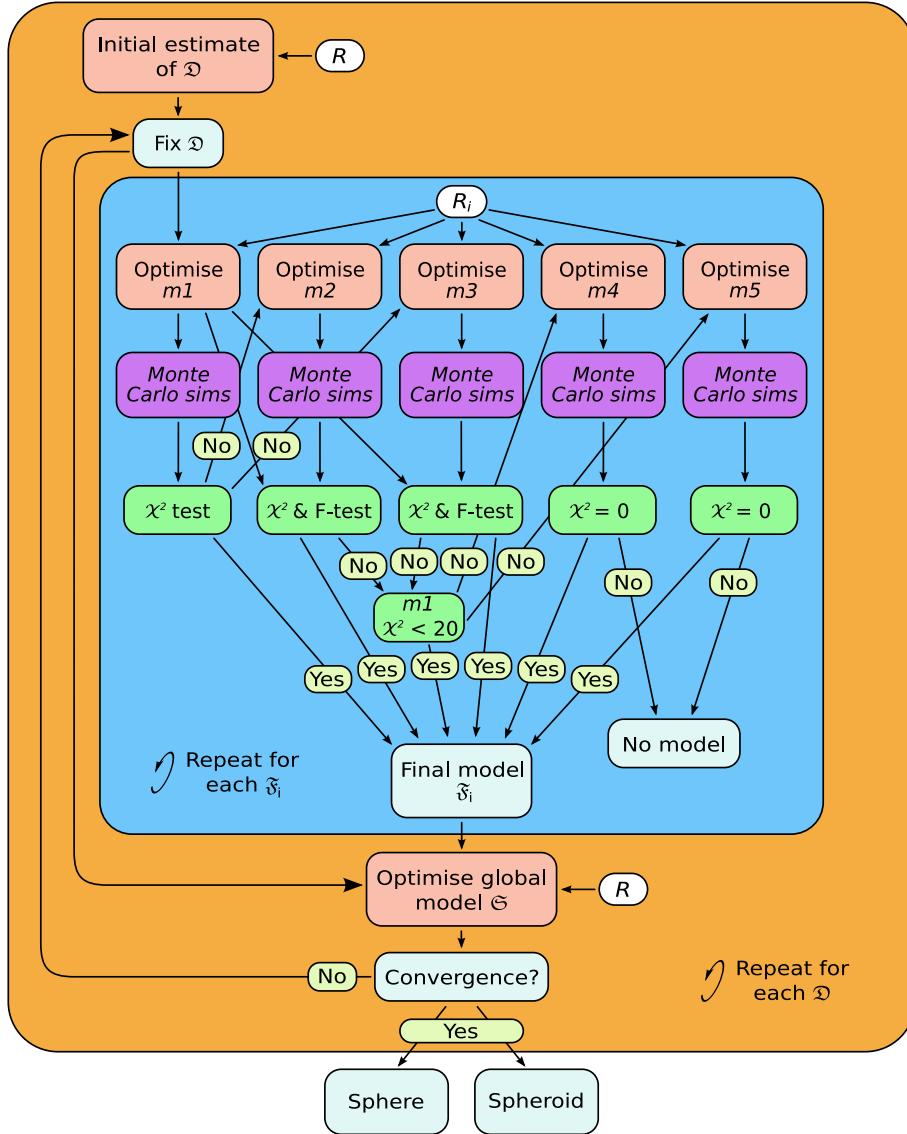


Figure 7.1: A schematic of the model-free optimisation protocol of [Mandel et al. \(1995\)](#). This specific protocol is for single field strength data. The initial diffusion tensor estimate is calculated using the R_2/R_1 ratio. The diffusion parameters of Ω are held constant while model-free models m_1 to m_5 ([7.21.1–7.21.5](#)) of the set \mathfrak{F}_i for each spin i are optimised and 500 Monte Carlo simulations executed. Using a web of ANOVA statistical tests, specifically χ^2 and F-tests, a step-up hypothesis testing model selection procedure is used to choose the best model-free model. These steps are repeated for all spins of the molecule. The global model S , the union of Ω and all \mathfrak{F}_i , is then optimised. These steps are repeated until convergence of the global model. The iterative process is repeated for both isotropic diffusion (sphere) and anisotropic diffusion (spheroid).

All of the data analysis techniques required for this protocol can be implemented within relax. The chi-squared distributions required for the chi-squared tests are constructed by Modelfree4 from the Monte Carlo simulations. If the optimisation algorithms and Monte Carlo simulations built into relax are utilised, then the relax script will need to construct the chi-squared distributions from the results as this is not yet coded into relax. The specific step-up hypothesis testing model selection of [Mandel et al. \(1995\)](#) is available through the `model_selection` user function. Coding the rest of the protocol into a script should be straightforward.

To implement this analysis, a number of scripts would need to be written. There is no sample script in relax for performing this analysis. The simple sample scripts from above would need to be extended. For example a starting script for determining the initial diffusion tensor estimates based on the R1/R2 ratio of [Kay et al. \(1989\)](#) would have to be written. The tensor from this script could then be feed into the `model_free/mf_multimodel.py` script, followed by the `model_free/modsel.py` script, and then a third script written to optimise the diffusion tensor. A master script could be written first run the initial diffusion tensor script, then to iteratively execute the last three scripts until convergence, and finally to select the best diffusion model (see Figure 7.1). Alternatively, these could all be combined into one super script.

7.6 The diffusion seeded paradigm

Ever since the original Lipari and Szabo papers ([Lipari and Szabo, 1982a,b](#)), the question of how to obtain the model-free description of the system has followed the route in which the diffusion tensor is initially estimated. Using this rough estimate, the model-free models are optimised for each spin system i , the best model selected, and then the global model \mathfrak{G} of the diffusion model \mathfrak{D} with each model-free model \mathfrak{F}_i is optimised. This procedure is then repeated using the diffusion tensor parameters of \mathfrak{G} as the initial input. Finally the global model is selected. The full protocol, when combined with AIC model selection ([d'Auvergne and Gooley, 2003](#)), is illustrated in Figure 7.2.

Again this protocol is not implemented in the relax sample scripts. This would have to be implemented in exactly the same manner as described in the previous section, but using the AIC model selection build into relax. Constructing this set of scripts, or a single master script, would be much easier than the [Mandel et al. \(1995\)](#) protocol as Modelfree4 would not need to be used, and the handling of F-tests and chi-squared tests is avoided.

7.7 The new model-free optimisation protocol

Here a new, fully automated model-free optimisation protocol will be presented. This protocol, defined in [d'Auvergne and Gooley \(2007\)](#) and [d'Auvergne and Gooley \(2008b\)](#), is significantly different from all those that came before, reversing the diffusion seeded paradigm as detailed below. Within relax it is referred to as the “new protocol” or the “d’Auvergne protocol”. The later name is to allow for more advanced protocols to be developed and added to relax by adventurous users in the future.

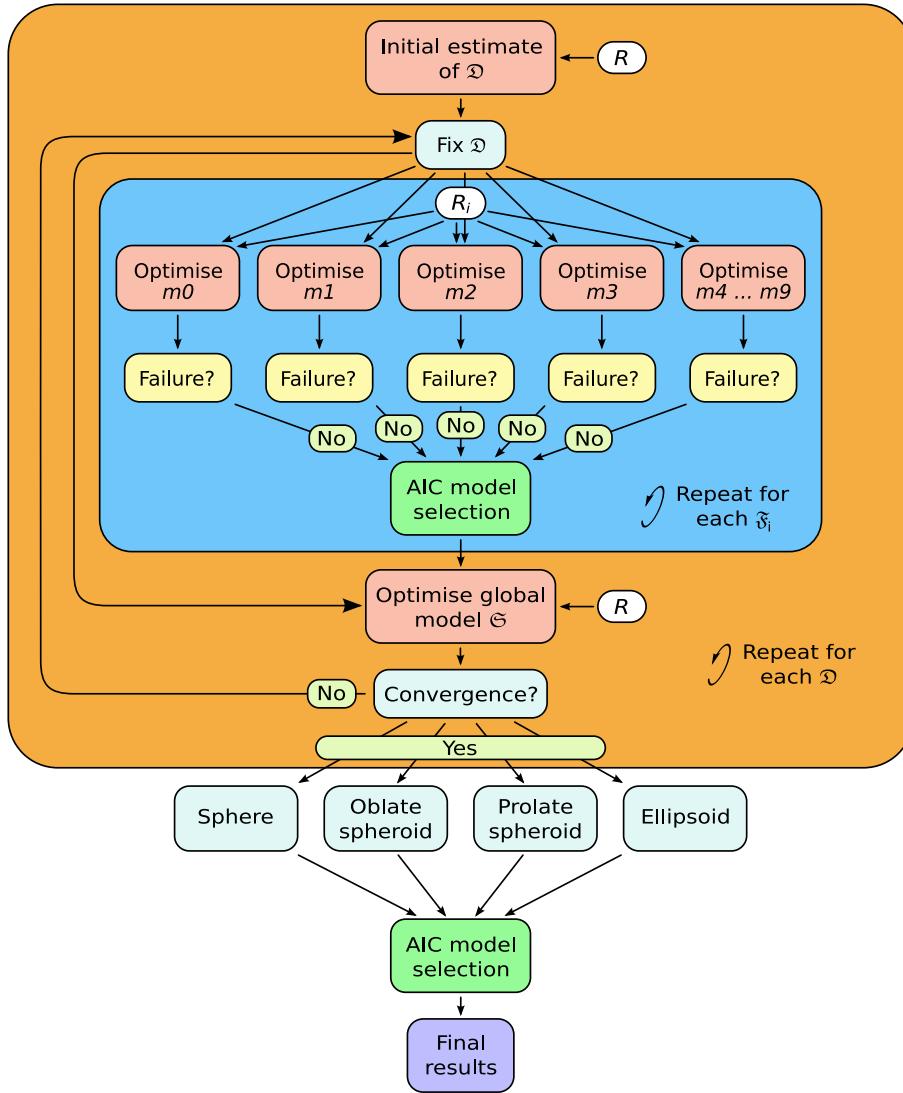


Figure 7.2: A schematic of model-free analysis using the diffusion seeded paradigm – the initial diffusion tensor estimate – together with AIC model selection and model elimination. The initial estimates of the parameters of Σ are held constant while model-free models m_0 to m_9 (7.21.0–7.21.9) of the set \mathfrak{F}_i for each spin system i are optimised, model elimination applied to remove failed models, and AIC model selection used to determine the best model. The global model Σ , the union of Σ and all \mathfrak{F}_i , is then optimised. These steps are repeated until convergence of the global model. The entire iterative process is repeated for each of the Brownian diffusion models. Finally AIC model selection is used to determine the best description of the dynamics of the molecule by selecting between the global models Σ including the sphere, oblate spheroid, prolate spheroid, and ellipsoid. Once the solution has been found, Monte Carlo simulations can be utilised for error analysis.

7.7.1 The new protocol – model-free models

The study of the dynamics of a macromolecule using model-free analysis to interpret the R_1 and R_2 relaxation rates together with the steady-state heteronuclear NOE brings two distinct, yet linked physical theories into play. The Brownian rotational diffusion of the molecule is the major contributor to relaxation. Although having less of an influence on relaxation the internal dynamics of individual nuclei within the molecule is nevertheless significant. The model-free description of the internal motion and the global diffusion of the entire molecule are theories which are linked due to their dependence on the same relaxation data. The model-free models for individual spin system constructed from the original and extended model-free theories ([Lipari and Szabo, 1982a,b](#); [Clore et al., 1990](#)) are assembled using parametric restrictions, the dropping of insignificant parameters, and the addition of the chemical exchange parameter R_{ex} . Labelled as $m0$ to $m9$ (Models 7.21.0–7.21.9 on page 87) these models are an extended list of those in ([Fushman et al., 1997](#); [Orekhov et al., 1999a](#); [Korzhnev et al., 2001](#); [Zhuravleva et al., 2004](#)).

7.7.2 The new protocol – the diffusion tensor

The ellipsoid

The most general form of Brownian rotational diffusion of macromolecules is the diffusion of an ellipsoid, a diffusion also labelled as asymmetric or fully anisotropic. This diffusion tensor can be fully specified by the geometric parameters \mathfrak{D}_x , \mathfrak{D}_y , and \mathfrak{D}_z , the eigenvalues of the tensor, as well as three orientational parameters, the Euler angles α , β , and γ . The diffusion equation for an ellipsoid was derived using the reasoning of [Einstein \(1905\)](#) in the two papers of [Perrin \(1934\)](#) and [Perrin \(1936\)](#). Following this, [Favro \(1960\)](#) unknowingly derived the same equations as presented in [Perrin \(1936\)](#) using a pseudo quantum mechanical approach. Borrowing heavily from [Perrin \(1936\)](#), [Woessner \(1962\)](#) derived the correlation function relevant for NMR relaxation of a bond vector rigidly attached to an ellipsoid. However these equations are not fully simplified and the parameter set $\{\mathfrak{D}_x, \mathfrak{D}_y, \mathfrak{D}_z, \alpha, \beta, \gamma\}$, the eigenvalues and Euler angles defining the tensor, is not optimally constructed for minimisation. A parameter shift to the set $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$, whereby the three geometric parameters are respectively the isotropic, anisotropic, and rhombic components of the diffusion tensor, drastically simplifies optimisation and is how the diffusion tensor is implemented within relax.

The spheroid

When two of the eigenvalues of the diffusion tensor are equal the molecule diffuses as a spheroid. This is also called axially symmetric anisotropic diffusion and can be described by the two geometric parameters \mathfrak{D}_{iso} and \mathfrak{D}_a together with the polar angle θ and azimuthal angle ϕ which define the unique axis of the diffusion tensor. Two classes of spheroid can be distinguished dependent on the relative values of the eigenvalues – the prolate and oblate spheroids. By using parametric constraints, both tensor types can be optimised within relax.

The sphere

The simplest form of diffusion occurs when all three eigenvalues are equal and the molecule diffuses as a sphere. This isotropic rotation can be characterised by the single parameter \mathfrak{D}_{iso} which is related to the global correlation time by the formula $1/\tau_m = 6\mathfrak{D}_{iso}$ ([Bloembergen et al., 1948](#)).

The local τ_m model-free models

Not only can the diffusion tensor be optimised as a global model affecting all spins of the molecule but a set of model-free models can be constructed in which each spin is assumed to diffuse independently. In these models a single local τ_m parameter approximates the true, multiexponential description of the Brownian rotational diffusion of the molecule. Each spin of the macromolecule is treated independently. Another set of model-free models which include the local τ_m parameter can be created and include $tm0$ to $tm9$ ([Models 7.22.0–7.22.9 on page 88](#)). These are simply models $m0$ to $m9$ with the local τ_m parameter added. These models are an extension of the ideas introduced in [Barbato et al. \(1992\)](#) and [Schurr et al. \(1994\)](#) whereby the model $tm2$, the original Lipari and Szabo model-free equation with a local τ_m parameter, is optimised to avoid issues with inaccurate diffusion tensor approximations.

Determination of the diffusion tensor from the local τ_m parameter

In [Brüschweiler et al. \(1995\)](#) and further investigated in [Lee et al. \(1997\)](#), a methodology for determining the diffusion tensor from the local τ_m parameter together with the orientation of the XH bond represented by the unit vector μ_i was presented. A local τ_m value was obtained for each spin i by optimising model $tm2$. The $\tau_{m,i}$ values were approximated using the quadric model

$$(6\tau_{m,i})^{-1} = \mu_i^T Q \mu_i, \quad (7.35)$$

where the eigenvalues of the matrix Q are defined as $Q_x = (\mathfrak{D}_y + \mathfrak{D}_z)/2$, $Q_y = (\mathfrak{D}_x + \mathfrak{D}_z)/2$, and $Q_z = (\mathfrak{D}_x + \mathfrak{D}_y)/2$. The diffusion tensor is then found by linear least-squares fitting.

7.7.3 The universal solution \mathfrak{U}

The complex model-free problem, in which the motions of each spin are both mathematically and statistically dependent on the diffusion tensor and vice versa, was formulated using set theory in [d'Auvergne and Gooley \(2007\)](#). This paper is important for understanding the entire concept of the new protocol in relax and for truly grasping the complexity of the model-free problem. The solution $\widehat{\mathfrak{U}}$ to the model-free problem was derived as an element of the universal set \mathfrak{U} , the union of the diverse model-free parameter spaces \mathfrak{S} . Each set \mathfrak{S} was constructed from the union of the model-free models \mathfrak{F} for all spins and the diffusion parameter set \mathfrak{D} . A single parameter loss on a single spin shifts optimisation to a different space \mathfrak{S} . Ever since the seminal work of [Kay et al. \(1989\)](#) the model-free problem has been tackled by first finding an initial estimate of the diffusion tensor and then determining the model-free dynamics of the system (see Sections [7.5](#) on page [95](#) and [7.6](#)

on page 97). This diffusion seeded paradigm is now highly evolved and much theory has emerged to improve this path to the solution $\widehat{\mathfrak{U}}$. The technique can, at times, suffer from a number of issues including the two minima problem of the spheroid diffusion tensor parameter space, the appearance of artificial chemical exchange (Tjandra et al., 1996), the appearance of artificial nanosecond motions (Schurr et al., 1994), and the hiding of internal nanosecond motions caused by the violation of the rigidity assumption (Orekhov et al., 1995b, 1999a,b).

7.7.4 Model-free analysis in reverse

A different approach was proposed in d'Auvergne and Gooley (2008b) for finding the universal solution $\widehat{\mathfrak{U}}$ of the extremely complex, convoluted model-free optimisation and modelling problem (d'Auvergne and Gooley, 2007), defined as

$$\widehat{\mathfrak{U}} = \hat{\theta} \in \left\{ \mathfrak{S} : \min_{\hat{\theta} \in \mathfrak{U}} \Delta_{K-L}(\hat{\theta}) \right\}, \quad \text{s.t. } \hat{\theta} = \arg \min \{ \chi^2(\theta) : \theta \in \mathfrak{S} \}. \quad (7.36)$$

This notation says that the minimised parameter vector within the space \mathfrak{S} which minimises the common Kullback-Leibler discrepancy Δ_{K-L} is selected from the universal set \mathfrak{U} as the universal solution $\widehat{\mathfrak{U}}$. The discrepancy of Kullback and Leibler (1951) is a measure of how well the model fits the data, in this case how well the global model \mathfrak{S} of the diffusion tensor together with the model-free models of all residues fits the relaxation data. This selection is subject to the condition that $\hat{\theta}$ is the argument or specific parameter vector which minimises the chi-squared function $\chi^2(\theta)$ such that θ is an element of the space \mathfrak{S} . Whereas the minimisation of the continuous chi-squared function within the single space \mathfrak{S} belongs to the mathematical field of optimisation (Nocedal and Wright, 1999), the selection of the universe \mathfrak{S} which minimises the discrepancy belongs to the statistical field of model selection (Akaike, 1973; Schwarz, 1978; Linhart and Zucchini, 1986; Zucchini, 2000; d'Auvergne and Gooley, 2003).

This new model-free optimisation protocol incorporates the ideas of the local τ_m model-free model (Barbato et al., 1992; Schurr et al., 1994) and the optimisation of the diffusion tensor using information from these models, analogously to the linear least-squares fitting of the quadric model (Brüschweiler et al., 1995; Lee et al., 1997). The protocol also follows the lead of the model-free optimisation protocol presented in Butterwick et al. (2004) whereby the diffusion seeded paradigm was reversed. Rather than starting with an initial estimation of the global diffusion tensor from the set \mathfrak{D} the protocol starts with the model-free parameters from \mathfrak{F} .

The first step of the Butterwick et al. (2004) protocol is the reduced spectral density mapping of Farrow et al. (1995). As R_{ex} has been eliminated from the analysis, three model-free models corresponding to $tm1$, $tm2$, and $tm5$ (Models 7.22.1, 7.22.2, and 7.22.5 on page 88) are employed. The model-free parameters are optimised using the reduced spectral density values and the best model is selected using F-tests. The spherical, spheroidal, and ellipsoidal diffusion tensors are obtained by linear least-squares fitting of the quadric model of Equation (7.35) using the local τ_m values (Brüschweiler et al., 1995; Lee et al., 1997). The best diffusion model is selected via F-tests and refined by iterative elimination of spins systems with high chi-squared values. This tensor is used to calculate local τ_m values for each spin system, approximating the multiexponential sum of the Brownian rotational diffusion correlation function with a single exponential, using the quadric model

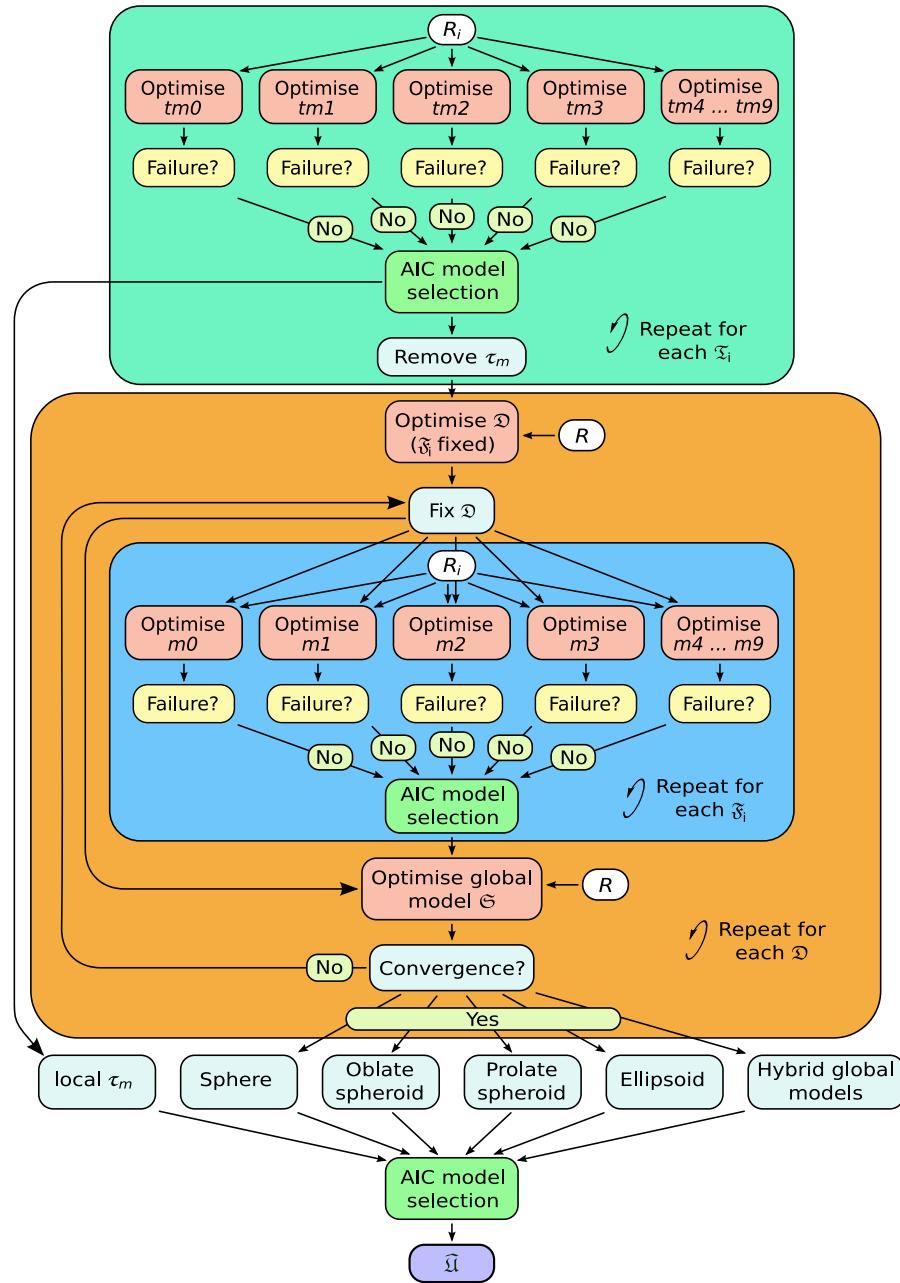


Figure 7.3: A schematic of the new model-free optimisation protocol. Initially models tm_0 to tm_9 (7.22.0–7.22.9) of the set \mathfrak{T}_i for each spin system i are optimised, model elimination used to remove failed models, and AIC model selection used to pick the best model. Once all the \mathfrak{T}_i have been determined for the system the the local τ_m parameter is removed, the model-free parameters are held fixed, and the global diffusion parameters of \mathfrak{D} are optimised. These parameters are used as input for the central part of the schematic which follows the same procedure as that of Figure 7.2. Convergence is however precisely defined as identical models \mathfrak{S} , identical χ^2 values, and identical parameters θ between two iterations. The universal solution $\hat{\mathfrak{U}}$, the best description of the dynamics of the molecule, is determined using AIC model selection to select between the local τ_m models for all spins, the sphere, oblate spheroid, prolate spheroid, ellipsoid, and possibly hybrid models whereby multiple diffusion tensors have been applied to different parts of the molecule.

of Equation (7.35). In the final step of the protocol these τ_m values are fixed and $m1$, $m2$, and $m5$ (Models 7.21.1, 7.21.2, and 7.21.5 on page 87) are optimised and the best model-free model selected using F-tests.

The new model-free protocol built into relax utilises the core foundation of the Butterwick et al. (2004) protocol yet its divergent implementation is designed to solve the universal equation of d'Auvergne and Gooley (2007) to find $\hat{\mathfrak{U}}$ (Equation 7.36). Models $tm0$ to $tm9$ (7.22.0–7.22.9 on page 88) in which no global diffusion parameters exist are employed to significantly collapse the complexity of the problem. Model-free minimisation (d'Auvergne and Gooley, 2008a), model elimination (d'Auvergne and Gooley, 2006), and then AIC model selection (Akaike, 1973; d'Auvergne and Gooley, 2003) can be carried out in the absence of the influence of global parameters. By removing the local τ_m parameter and holding the model-free parameter values constant these models can then be used to optimise the diffusion parameters of \mathfrak{D} . Model-free optimisation, model elimination, AIC model selection, and optimisation of the global model \mathfrak{G} is iterated until convergence. The iterations allow for sliding between different universes \mathfrak{G} to enable the collapse of model complexity, to refine the diffusion tensor, and to find the solution within the universal set \mathfrak{U} . The last step is the AIC model selection between the different diffusion models. Because the AIC criterion approximates the Kullback-Leibler discrepancy (Kullback and Leibler, 1951), central to the universal solution of Equation (7.36), it was chosen for all three model selection steps over BIC model selection (Schwarz, 1978; d'Auvergne and Gooley, 2003; Chen et al., 2004). The new protocol avoids the problem of under-fitting whereby artificial motions appear, avoids the problems involved in finding the initial diffusion tensor within \mathfrak{D} , and avoids the problem of hidden internal nanosecond motions and the inability to slide between universes to get to $\hat{\mathfrak{U}}$ (see d'Auvergne and Gooley (2007) for more details). The full protocol is summarised in Figure 7.3.

7.8 The new protocol in the prompt/script UI mode

7.8.1 d'Auvergne protocol script mode – the sample script

The sample script for performing this new analysis is `sample_scripts/model_free/dauvergne_protocol.py`. The full script is replicated below. The docstring at the start of the script explains the practical implementation of the full protocol. If your copy of the `dauvergne_protocol.py` script taken from the same relax version as this manual does not match the text below, please contact the relax developers via the relax-devel mailing list (see section [3.2.3](#) on page [30](#)). To use this script, copy it to a dedicated directory containing your PDB file and relaxation data files. The protocol will produce many files and directories, so it is best that these are placed within a dedicated results directory. The contents of the script are:

```
28
29      d'Auvergne, E. J. and Gooley, P. R. (2007). Set theory formulation of the model-free
      problem and the diffusion seeded model-free paradigm. 3(7), 483-494.
30
31      The basic three references for the original and extended model-free theories are:
32
33      Lipari, G. and Szabo, A. (1982a). Model-free approach to the interpretation of nuclear
      magnetic-resonance relaxation in macromolecules I. Theory and range of validity. J.
      Am. Chem. Soc., 104(17), 4546-4559.
34
35      Lipari, G. and Szabo, A. (1982b). Model-free approach to the interpretation of nuclear
      magnetic-resonance relaxation in macromolecules II. Analysis of experimental results.
      J. Am. Chem. Soc., 104(17), 4559-4570.
36
37      Clore, G. M., Szabo, A., Bax, A., Kay, L. E., Driscoll, P. C., and Gronenborn, A.M.
      (1990). Deviations from the simple 2-parameter model-free approach to the
      interpretation of N-15 nuclear magnetic-relaxation of proteins. J. Am. Chem. Soc.,
      112(12), 4989-4991.
38
39
40      How to use this script
41      =====
42
43      The value of the variable DIFF_MODEL will determine the behaviour of this script. The
      five diffusion models used in this script are:
44
45      Model I (MI) - Local tm.
46      Model II (MII) - Sphere.
47      Model III (MIII) - Prolate spheroid.
48      Model IV (MIV) - Oblate spheroid.
49      Model V (MV) - Ellipsoid.
50
51      Model I must be optimised prior to any of the other diffusion models, while the Models II
      to V can be optimised in any order. To select the various models, set the variable
      DIFF_MODEL to the following strings:
52
53      MI - 'local_tm'
54      MII - 'sphere'
55      MIII - 'prolate'
56      MIV - 'oblate'
57      MV - 'ellipsoid'
58
59      This approach has the advantage of eliminating the need for an initial estimate of a
      global diffusion tensor and removing all the problems associated with the initial
      estimate.
60
61      It is important that the number of parameters in a model does not exceed the number of
      relaxation data sets for that spin. If this is the case, the list of models in the
      MF_MODELS and LOCAL_TM_MODELS variables will need to be trimmed.
62
63
64      Model I - Local tm
65      =====
66
67      This will optimise the diffusion model whereby all spin of the molecule have a local tm
      value, i.e. there is no global diffusion tensor. This model needs to be optimised
      prior to optimising any of the other diffusion models. Each spin is fitted to the
      multiple model-free models separately, where the parameter tm is included in each
      model.
68
69      AIC model selection is used to select the models for each spin.
```

```

70
71
72 Model II - Sphere
~~~~~
73
74
75 This will optimise the isotropic diffusion model. Multiple steps are required, an initial
    optimisation of the diffusion tensor, followed by a repetitive optimisation until
    convergence of the diffusion tensor. Each of these steps requires this script to be
    rerun. For the initial optimisation, which will be placed in the directory './sphere/
    init/', the following steps are used:
76
77 The model-free models and parameter values for each spin are set to those of diffusion
    model MI.
78
79 The local tm parameter is removed from the models.
80
81 The model-free parameters are fixed and a global spherical diffusion tensor is minimised.
82
83
84 For the repetitive optimisation, each minimisation is named from 'round_1' onwards. The
    initial 'round_1' optimisation will extract the diffusion tensor from the results file
    in './sphere/init/', and the results will be placed in the directory './sphere/
    round_1/'. Each successive round will take the diffusion tensor from the previous
    round. The following steps are used:
85
86 The global diffusion tensor is fixed and the multiple model-free models are fitted to each
    spin.
87
88 AIC model selection is used to select the models for each spin.
89
90 All model-free and diffusion parameters are allowed to vary and a global optimisation of
    all parameters is carried out.
91
92
93 Model III - Prolate spheroid
~~~~~
94
95
96 The methods used are identical to those of diffusion model MII, except that an axially
    symmetric diffusion tensor with  $Da \geq 0$  is used. The base directory containing all
    the results is './prolate/'.
97
98
99 Model IV - Oblate spheroid
~~~~~
100
101
102 The methods used are identical to those of diffusion model MII, except that an axially
    symmetric diffusion tensor with  $Da \leq 0$  is used. The base directory containing all
    the results is './oblate/'.
103
104
105 Model V - Ellipsoid
~~~~~
106
107
108 The methods used are identical to those of diffusion model MII, except that a fully
    anisotropic diffusion tensor is used (also known as rhombic or asymmetric diffusion).
    The base directory is './ellipsoid/'.
109
110
111
112 Final run
~~~~~
113

```

```

114
115 Once all the diffusion models have converged, the final run can be executed. This is done
116 by setting the variable DIFF_MODEL to 'final'. This consists of two steps, diffusion
117 tensor model selection, and Monte Carlo simulations. Firstly AIC model selection is
118 used to select between the diffusion tensor models. Monte Carlo simulations are then
119 run solely on this selected diffusion model. Minimisation of the model is bypassed as
120 it is assumed that the model is already fully optimised (if this is not the case the
121 final run is not yet appropriate).
122
123 The final black-box model-free results will be placed in the file 'final/results'.
124 """
125
126 # Python module imports.
127 from time import asctime, localtime
128
129 # relax module imports.
130 from auto_analyses.dauvergne_protocol import dAuvergne_protocol
131
132
133 # Analysis variables.
134 #####
135
136 # The diffusion model.
137 DIFF_MODEL = 'local_tm'
138
139 # The model-free models. Do not change these unless absolutely necessary, the protocol is
140 # likely to fail if these are changed.
141 MF_MODELS = ['m0', 'm1', 'm2', 'm3', 'm4', 'm5', 'm6', 'm7', 'm8', 'm9']
142 LOCAL_TM_MODELS = ['tm0', 'tm1', 'tm2', 'tm3', 'tm4', 'tm5', 'tm6', 'tm7', 'tm8', 'tm9']
143
144 # The grid search size (the number of increments per dimension).
145 GRID_INC = 11
146
147 # The optimisation technique.
148 MIN_ALGOR = 'newton'
149
150 # The number of Monte Carlo simulations to be used for error analysis at the end of the
151 # analysis.
152 MC_NUM = 500
153
154 # Automatic looping over all rounds until convergence (must be a boolean value of True or
155 # False).
156 CONV_LOOP = True
157
158
159 # Set up the data pipe.
160 #####
161
162 # The following sequence of user function calls can be changed as needed.
163
164 # Create the data pipe.
165 pipe_bundle = "mf (%s)" % asctime(localtime())
166 name = "origin - " + pipe_bundle
167 pipe.create(name, 'mf', bundle=pipe_bundle)
168
169 # Load the PDB file.
170 structure.read_pdb('1f3y.pdb', set_mol_name='Ap4Aase', read_model=3)
171
172 # Set up the 15N and 1H spins (both backbone and Trp indole sidechains).
173 structure.load_spins('@N', ave_pos=True)

```

```

166 structure.load_spins('@NE1', ave_pos=True)
167 structure.load_spins('@H', ave_pos=True)
168 structure.load_spins('@HE1', ave_pos=True)
169 spin.isotope('15N', spin_id='@N*')
170 spin.isotope('1H', spin_id='@H*')
171
172 # Set up the 15N spins (alternative to the structure-based approach).
173 #sequence.read(file='noe.500.out', dir=None, mol_name_col=1, res_num_col=2, res_name_col
174 =3, spin_num_col=4, spin_name_col=5)
175 #spin.element(element='N', spin_id='@N*')
176 #spin.isotope('15N', spin_id='@N*')
177
178 # Generate the 1H spins for the magnetic dipole-dipole relaxation interaction (alternative
179 # to the structure-based approach).
180 #sequence.attach_protons()
181
182 # Load the relaxation data.
183 relax_data.read(ri_id='R1_600', ri_type='R1', frq=599.719*1e6, file='r1.600.out',
184 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
185 data_col=6, error_col=7)
186 relax_data.read(ri_id='R2_600', ri_type='R2', frq=599.719*1e6, file='r2.600.out',
187 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
188 data_col=6, error_col=7)
189 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=599.719*1e6, file='noe.600.out',
190 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
191 data_col=6, error_col=7)
192 relax_data.read(ri_id='R1_500', ri_type='R1', frq=500.208*1e6, file='r1.500.out',
193 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
194 data_col=6, error_col=7)
195 relax_data.read(ri_id='R2_500', ri_type='R2', frq=500.208*1e6, file='r2.500.out',
196 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
197 data_col=6, error_col=7)
198 relax_data.read(ri_id='NOE_500', ri_type='NOE', frq=500.208*1e6, file='noe.500.out',
199 mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
200 data_col=6, error_col=7)
201
202 # Deselect spins to be excluded (including unresolved and specifically excluded spins).
203 deselect.read(file='unresolved', dir=None, spin_id_col=None, mol_name_col=1, res_num_col
204 =2, res_name_col=3, spin_num_col=4, spin_name_col=5, sep=None, spin_id=None, boolean='
205 AND', change_all=False)
206 deselect.read(file='exclude', spin_id_col=1)
207
208 # Define the magnetic dipole-dipole relaxation interaction.
209 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
210 interatom.define(spin_id1='@NE1', spin_id2='@HE1', direct_bond=True)
211 interatom.set_dist(spin_id1='@N*', spin_id2='@H*', ave_dist=1.02 * 1e-10)
212 interatom.unit_vectors()
213
214 # Define the chemical shift relaxation interaction.
215 value.set(-172 * 1e-6, 'csa', spin_id='@N*')
216
217
218 # Execution.
219 ######
220
221 # Do not change!
222 dAuvergne_protocol(pipe_name=name, pipe_bundle=pipe_bundle, diff_model=DIFF_MODEL,
223 mf_models=MF_MODELS, local_tm_models=LOCAL_TM_MODELS, grid_inc=GRID_INC, min_algor=
224 MIN_ALGOR, mc_sim_num=MC_NUM, conv_loop=CONV_LOOP)

```

7.8.2 d'Auvergne protocol script mode – analysis variables

At the start of the script you will notice a number of **Analysis variables**. Unless you know what you are doing, you should only change the DIFF_MODEL variable to the following:

'local_tm': This is the first diffusion model which must be optimised prior to optimising any of the other diffusion models. It consists of the local τ_m models (equations 7.22.0 to 7.22.9 on page 88).

'sphere': This second diffusion model is that of isotropic Brownian diffusion.

'prolate': This third diffusion model is that of the prolate axially-symmetric rotor.

'oblate': This fourth diffusion model is that of the oblate axially-symmetric rotor.

'ellipsoid': This fifth diffusion model is that of fully rhombic Brownian diffusion (see Perrin (1934, 1936) for the original theory).

'final': This is a special value which will finalise the analysis by selecting the best diffusion model to describe your system and to perform Monte Carlo simulations for error propagation.

The MF_MODELS and LOCAL_TM_MODELS variables specify which model-free models will be used in the analysis. But, as the full protocol behind this script which is designed to find the solution of the universal set \mathfrak{U} (see section 7.7.2 on page 100) expects that all these models are present, you should not change these variables. If you do remove some model-free models, you should fully expect to see artificial motions which you will not be able to distinguish from the real molecular motions.

The next variables GRID_INC and MIN_ALGOR are related to the optimisation of the model-free models. These should also not be touched unless you fully understand the consequences (and have read d'Auvergne and Gooley (2008a)). The variable MC_NUM specifies the number of Monte Carlo simulations. This number can be increased but, for realistic parameter errors in your publication, it should not set lower than 500 simulations.

Finally the CONV_LOOP variable is designed to make your life easier. If left at the value of True, the script will iterate until convergence (see Figure 2 in d'Auvergne and Gooley (2008b) to understand this concept). If changed to False, then you will need to run the script manually for the 15 or so iterations of each diffusion model, and then repeat this for all diffusion models II to V.

7.8.3 d'Auvergne protocol script mode – data pipe initialisation

The next part of the script between the **Analysis variables** and execution sets up a data pipe with all of the spin information and relaxation data to pass into the automated protocol. The data pipe is created in the lines:

```
156 # Create the data pipe.
157 pipe_bundle = "mf (%s)" % asctime(localtime())
158 name = "origin - " + pipe_bundle
159 pipe.create(name, 'mf', bundle=pipe_bundle)
```

Firstly a data pipe bundle name is created containing the date and time at the point the script is first executed. This pipe bundle is used to group together all of the data pipes created automatically by the protocol. See section 4.2.1 on page 34 for more details.

The data pipe name used for this initial setup is set to `origin - mf (x)` where `x` is the data and time again. This name is unique and will not clash with the data pipes created within the protocol. The `pipe.create` command will create the data pipe and add it to a new pipe bundle.

7.8.4 d'Auvergne protocol script mode – setting up the spin systems

To see how to set up the spin system data in all possible situations, please see Chapter 4 for a thorough description. Here two different methods are presented. The first is by extracting the spins from a PDB file which is first loaded with:

```
161 # Load the PDB file.
162 structure.read_pdb('1f3y.pdb', set_mol_name='Ap4Aase', read_model=3)
```

This will read the 3rd model from the 1F3Y PDB file and name the single molecule as ‘Ap4Aase’. The ¹⁵N and ¹H spins for the backbone and tryptophan indole sidechain are extracted from the structure with the user functions:

```
164 # Set up the 15N and 1H spins (both backbone and Trp indole sidechains).
165 structure.load_spins('@N', ave_pos=True)
166 structure.load_spins('@NE1', ave_pos=True)
167 structure.load_spins('@H', ave_pos=True)
168 structure.load_spins('@HE1', ave_pos=True)
```

As the PDB file does not contain isotope information, this is set with the user functions:

```
169 spin.isotope('15N', spin_id='@N*')
170 spin.isotope('1H', spin_id='@H*')
```

The spin ID ‘@N*’ uses regular expression and will match both the ‘N’ and ‘NE1’ spins.

The alternative approach is if a structure is missing. This is the commented out code:

```
172 # Set up the 15N spins (alternative to the structure-based approach).
173 sequence.read(file='noe.500.out', dir=None, mol_name_col=1, res_num_col=2, res_name_col=3,
    spin_num_col=4, spin_name_col=5)
174 spin.element(element='N', spin_id='@N*')
175 spin.isotope('15N', spin_id='@N*')
176
177 # Generate the 1H spins for the magnetic dipole-dipole relaxation interaction (alternative
    to the structure-based approach).
178 sequence.attach_protons()
```

To use this, you will need to place comments (the # character) in front of the previous `structure.read_pdb`, `structure.load_spins` and `spin.isotope` user functions. Then uncomment the `sequence.read`, `spin.element`, `spin.isotope` and `sequence.attach_protons` user functions. The ¹⁵N spins will be extracted from the `noe.500.out` file. The `spin.element` and `spin.isotope` user functions set the information required for relax to understand which relaxation mechanisms are active. Finally the `sequence.attach_protons` user function will automatically attach protons to all nitrogen spin systems. As

this method is devoid of atomic positional information, the N-H bonds are absent and the diffusion models requiring structural information (the spheroids and ellipsoid) must be skipped.

7.8.5 d'Auvergne protocol script mode – loading the data

The next step is to load the relaxation data for each spin system. The sample script assumes that the NOE, R₁ and R₂ data was generated using relax. One of the six user function calls is:

```
180 # Load the relaxation data.
181 relax_data.read(ri_id='R1_600', ri_type='R1', frq=599.719*1e6, file='r1.600.out',
182     mol_name_col=1, res_num_col=2, res_name_col=3, spin_num_col=4, spin_name_col=5,
183     data_col=6, error_col=7)
```

This pattern is repeated for all of the relaxation data files loaded. The important points are that each relaxation data set must have its own unique identification string (`ri_id`), the relaxation data type specified (`ri_type`) and the frequency in Hertz (not MHz) specified. Note that the frequency must be the exact value – see the `sfrq` parameter in the Varian `procpar` file or the `SF01` parameter in the Bruker `acqus` file.

7.8.6 d'Auvergne protocol script mode – deselection

The sample script now presents the deselection of spins using two different files:

```
188 # Deselect spins to be excluded (including unresolved and specifically excluded spins).
189 deselect.read(file='unresolved', dir=None, spin_id_col=None, mol_name_col=1, res_num_col
190     =2, res_name_col=3, spin_num_col=4, spin_name_col=5, sep=None, spin_id=None, boolean='
191     AND', change_all=False)
190 deselect.read(file='exclude', spin_id_col=1)
```

The `unresolved` file contains a list of spins which are unresolved in all spectra. If relax has been used for calculating the NOE and fitting the relaxation curves, then this step is not needed as the relaxation data files will not have any data for the spins deselected in those analyses. The second file `exclude` is a list of spin ID strings (see section 4.2.2 on page 36) of spins that for ever reason are to be excluded from the analysis.

7.8.7 d'Auvergne protocol script mode – relaxation interactions

The next step is to fully specify all of the relaxation interactions active on the spins of interest. Firstly the magnetic dipole-dipole interaction is defined between directly bonded nitrogens and protons:

```
192 # Define the magnetic dipole-dipole relaxation interaction.
193 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
194 interatom.define(spin_id1='@NE1', spin_id2='@HE1', direct_bond=True)
195 interatom.set_dist(spin_id1='@N*', spin_id2='@H*', ave_dist=1.02 * 1e-10)
196 interatom.unit_vectors()
```

The regular expression ‘@N*’ and ‘@H*’ cannot be used with the `dipole_pair.` `define` user function as otherwise @N spins will be connected to @HE1 spins of the same tryptophan residue and @H spins to @NE1 spins. The average interatomic distance is set to 1.02 Ångstrom (though the `dipole_pair.set_dist` user function expects the units of meters). The `dipole_pair.unit_vectors` is used to calculate the averaged unit vector between the two atoms.

Secondly the chemical shift anisotropy (CSA) relaxation mechanism is defined via the single command:

```
198 # Define the chemical shift relaxation interaction.
199 value.set(-172 * 1e-6, 'csa', spin_id='@N*')
```

If your system does not experience CSA relaxation, the value can be set to zero.

7.8.8 d'Auvergne protocol script mode – execution

Once the data is set up and you have modified your script to match your analysis needs, then the data pipe, pipe bundle and analysis variables are passed into the `dAuvergne_protocol` class. This is the final line of the script:

```
203 # Execution.
204 #####
205
206 # Do not change!
207 dAuvergne_protocol(pipe_name=name, pipe_bundle=pipe_bundle, diff_model=DIFF_MODEL,
    mf_models=MF_MODELS, local_tm_models=LOCAL_TM_MODELS, grid_inc=GRID_INC, min_algor=
    MIN_ALGOR, mc_sim_num=MC_NUM, conv_loop=CONV_LOOP)
```

This script needs to be executed multiple times, once for each of the diffusion models. For example if the `DIFF_MODEL` variable is set to ‘ellipsoid’, you can run relax with:

```
$ relax --tee log.ellipsoid dauvergne_protocol.py
```

You should use a different log file for each diffusion model, though relax will prevent you from overwriting an old log file. Note that the `log.*` files for each diffusion model may end up being a few gigabytes in size.

For a full analysis of a protein system, the analysis may require between one to two weeks to complete. This can be speed up using Gary Thompson’s multi-processor code (see section 1.3 on page 17). The analysis is performed as described in the previous sections and summarised in Figure 7.3. If you are curious, the implementation is within a very large relax script called `auto_analyses/dauvergne_protocol.py` (which must never be changed). This automatic analysis script hides all of the complexity of the full protocol from the sample script.

7.9 The new protocol in the GUI

A model-free analysis can be performed within the GUI (see Figure 1.8 on page 18). This analysis is that of the fully automated d’Auvergne protocol which can be chosen via the analysis selection wizard (Figure 1.4 on page 12). Please see Section 7.7 on page 97 for a description of this new model-free protocol.

The GUI is designed to be robust – you should be able to set up all the input data and parameters in any order with relax returning you warnings if something is missing. The analysis will only execute once everything is correctly set up. If this is not the case, clicking on the “Execute relax” button will display a warning window explaining what the issue is rather than initialising the analysis. Despite the self-explanatory nature of the GUI a tutorial on how to use the GUI, with screenshots, will be presented below.

If the “Protocol mode” field is left to the “Fully automated” setting then, after clicking on “Execute relax”, the calculation can be left to complete. It is highly recommended to check the log messages in the relax controller window, at least at the start of the analysis, to make sure that all the data is being read correctly and everything is set up as desired. All warnings should be carefully checked as these can indicate a fatal problem. If you would like to log all the messages into a file, relax can be run with:

```
$ relax -g --log log
```

Note that the size of this `log` file could end up being in the gigabyte range for a model-free analysis.

For the full analysis to complete, for a protein system this may take about a week. Depending on the nature of the problem and the speed of the computer, the calculation time may be significantly shorter or longer. To speed up the calculations, if you have access to multiple cores and/or hyper-threading, the GUI can be run using Gary Thompson’s multi-processor framework (see section 1.3 on page 17). For example on a dual-core, dual-CPU system, four calculations can be run simultaneously. In this case, the GUI can be launched with:

```
$ mpirun -np 5 /usr/local/bin/relax --multi='mpi4py' --gui --log log
```

This assumes that OpenMPI and the Python `mpi4py` module have been installed on your system, and relax is installed into the `/usr/local/bin/` directory. If this is successful, you should only see a single relax GUI window (and not five windows) and in the relax controller, you should see text similar to:

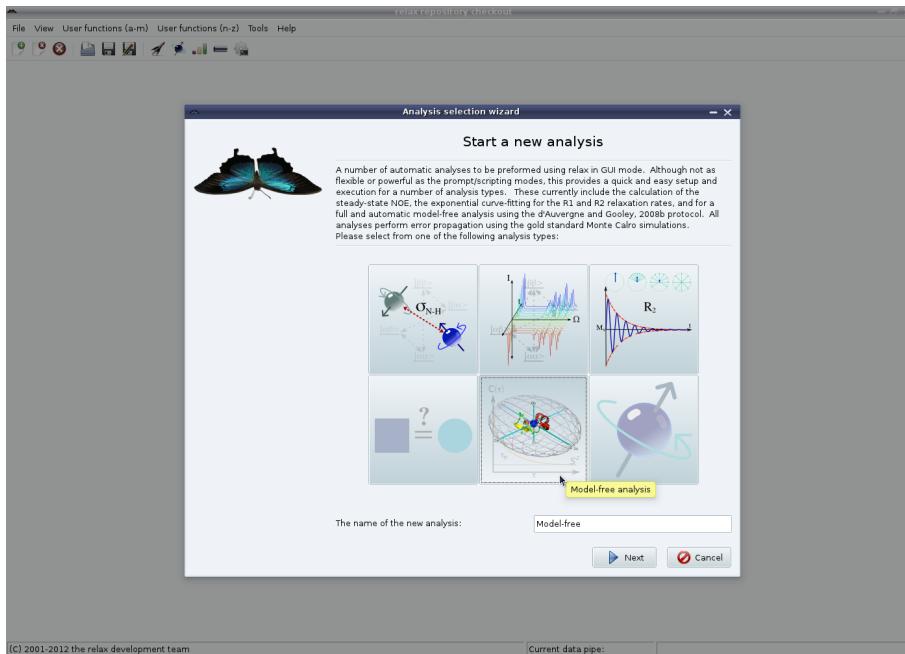
```
Processor fabric: MPI 2.1 running via mpi4py with 4 slave processors & 1 master. Using
Open MPI 1.4.3.
```

If you are using a different MPI implementation, please see the documentation of that implementation to see how to launch a program in MPI mode. Finally as the calculation takes so long, we will run the calculations at a lower priority so that the computer is not slowed down too much and remains responsive. Therefore this model-free GUI analysis tutorial will be launched with the full command:

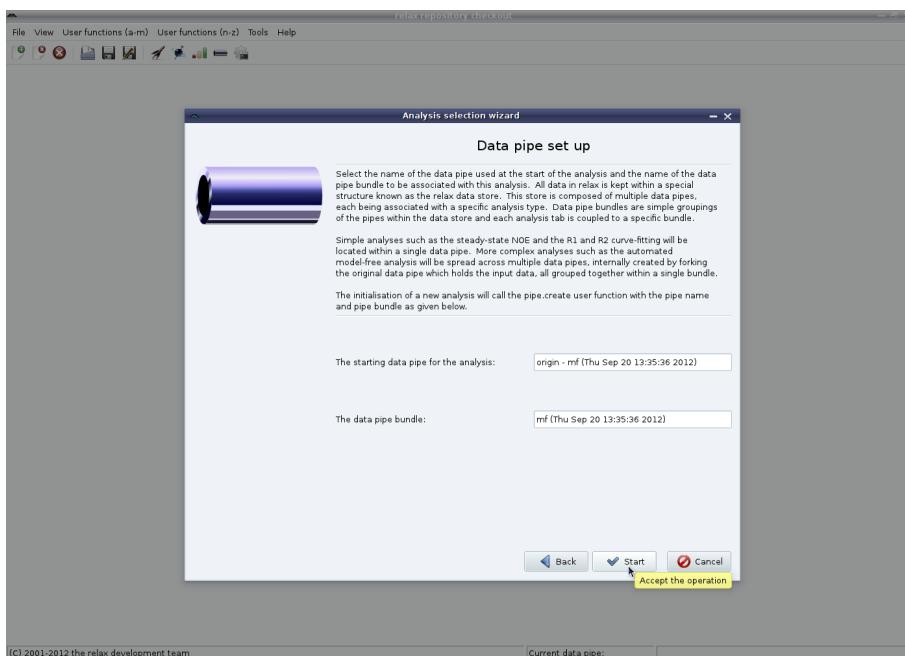
```
$ nice -n 15 mpirun -np 5 /usr/local/bin/relax --multi='mpi4py' --gui --log log
```

7.9.1 d'Auvergne protocol GUI mode – data pipe initialisation

First launch the analysis selection wizard (see Figure 1.4 on page 12) and click on the model-free analysis button.

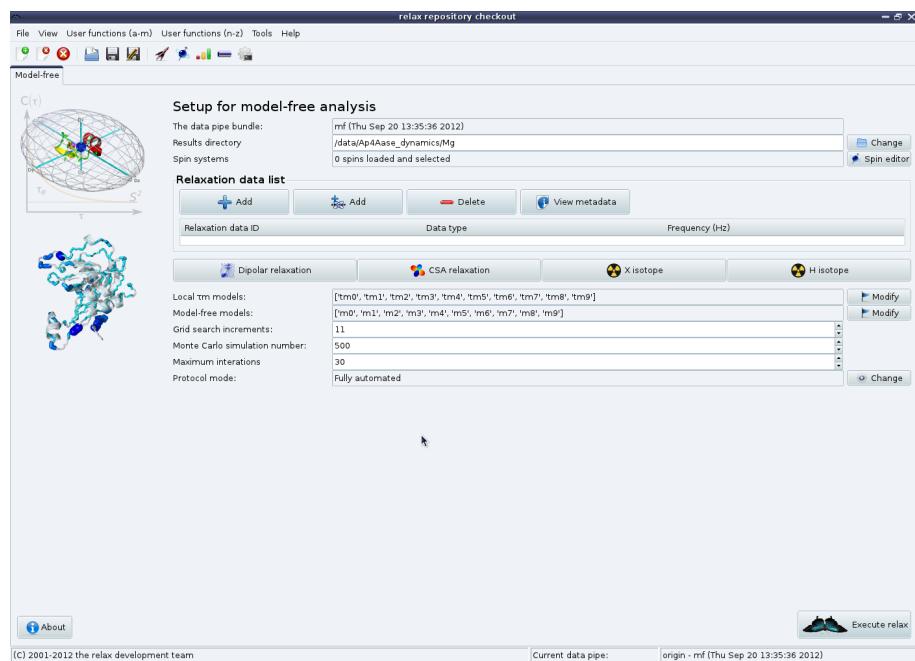


Click on the “Next” button and on the second page click on the “Start” button. The text in the second page need not be changed.

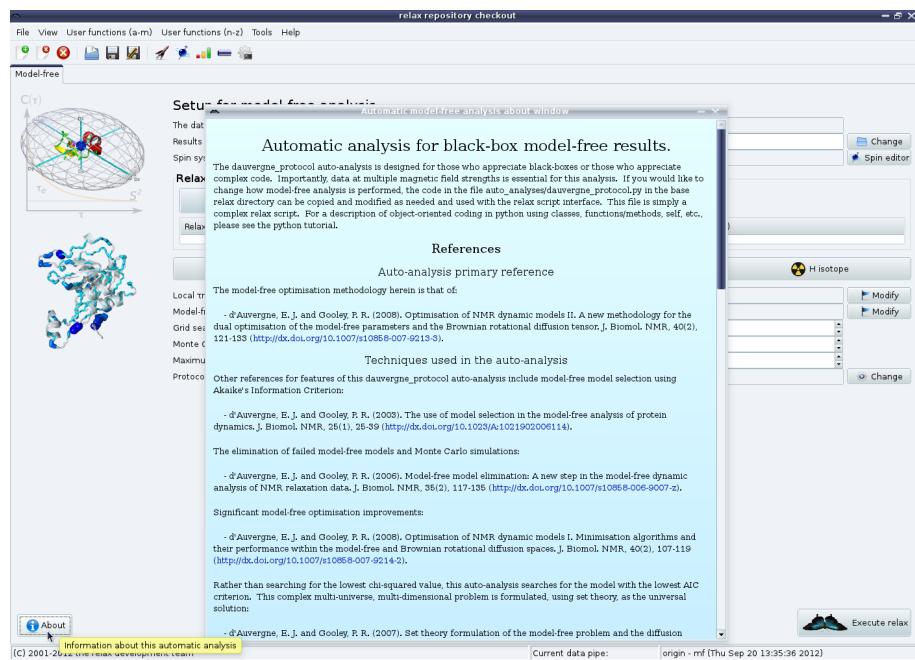


7.9.2 d'Auvergne protocol GUI mode – general setup

Once the analysis is initialised, the screen should look like:



The “About” button in the bottom left will bring up a window with the same description as given in the sample script:



At this point, back in the main relax window, the results directory where all of the output files and directories will be saved can be changed.

7.9.3 d'Auvergne protocol GUI mode – setting up the spin systems

The model-free dynamics is at the level of the spins – relaxation affects individual nuclei. In the main model-free tab you will see the “Spin systems” GUI element. Clicking on the “Spin editor” button to the right of this element will launch the spin editor window.

In this tutorial, the 3rd model of the PDB file 1f3y.pdb will be used to extract the spin system information. The molecule will be named “Ap4Aase”. For details on how to create the spin containers necessary for this analysis, please see section 4.5.2 on page 40 (or analyses lacking structural data in section 4.5.3 on page 43 for sequence files).

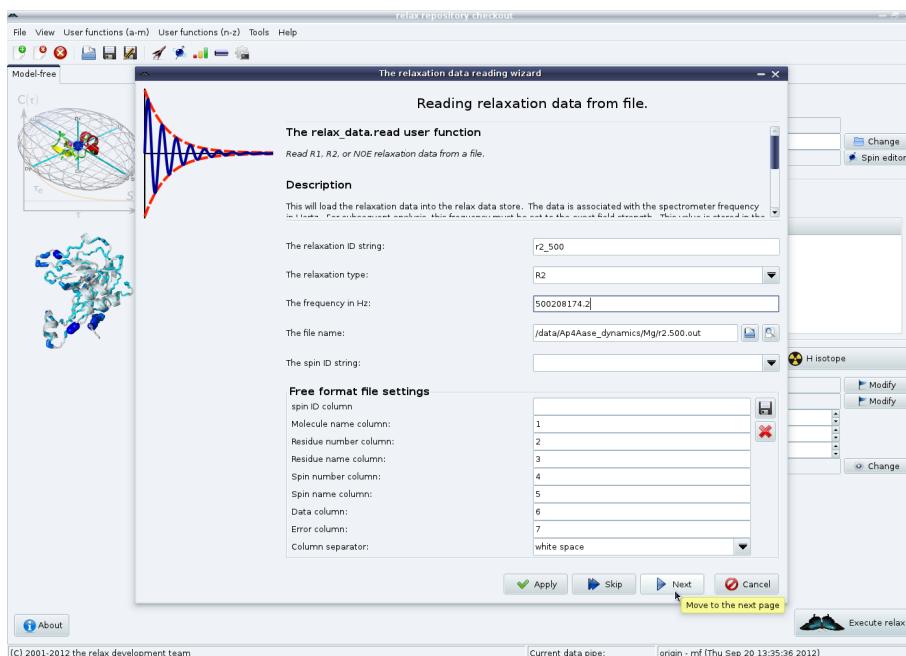
Note that for this tutorial, the protein backbone spins “¹³CN” and “¹³CH” as well as the tryptophan sidechain indole “¹⁵NE1” and “¹⁵HE1” spins should be loaded in the spin viewer window.

7.9.4 d’Auvergne protocol GUI mode – unresolved spins

To deselect all unwanted spins, please read section 4.5.5 on page 44 for all the necessary instructions for how to do this in the GUI.

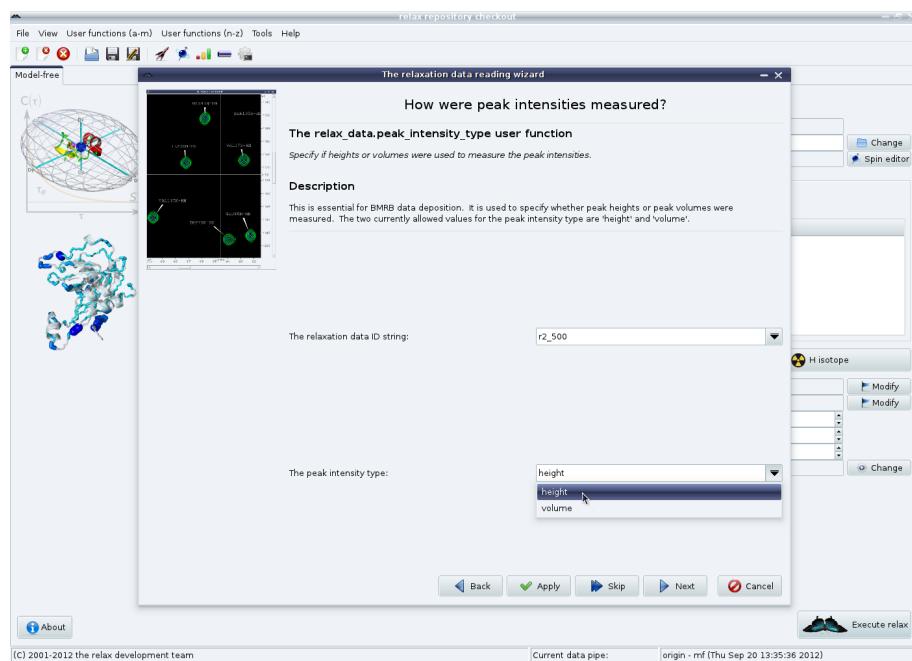
7.9.5 d’Auvergne protocol GUI mode – loading the data

The relaxation data can either come from plain columnar formatted text files (such as if relax was used for the NOE, R₁ and R₂ analyses) or from the Bruker Dynamics Centre. For the former, click on the “Add” button in the “Relaxation data list” GUI element. This route will be used for this tutorial. For the later, click on the “Add Bruker” button. After clicking on “Add”, you will see the relaxation data loading wizard:



In this first page, the unique relaxation data identification string (“r2_500”), the relaxation data type (“R2”), the frequency in Hertz (“500208174.2”) and the file (“r2.500.out”) are specified. If your data comes from another program, you may need to change the values in the “Free format file settings” element. Click on “Next” to load the data from the file.

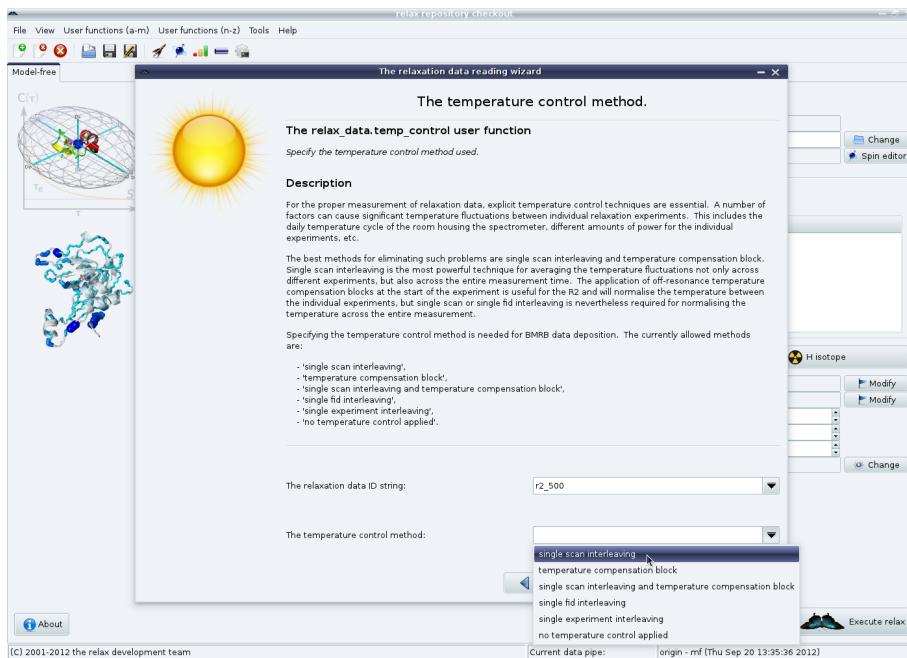
The next wizard pages are for loading the metadata which is used in the BioMagResBank deposition of your final results. The first is how the peak intensities were measured, either peak heights or volumes. Select the appropriate value, then click on “Next”.



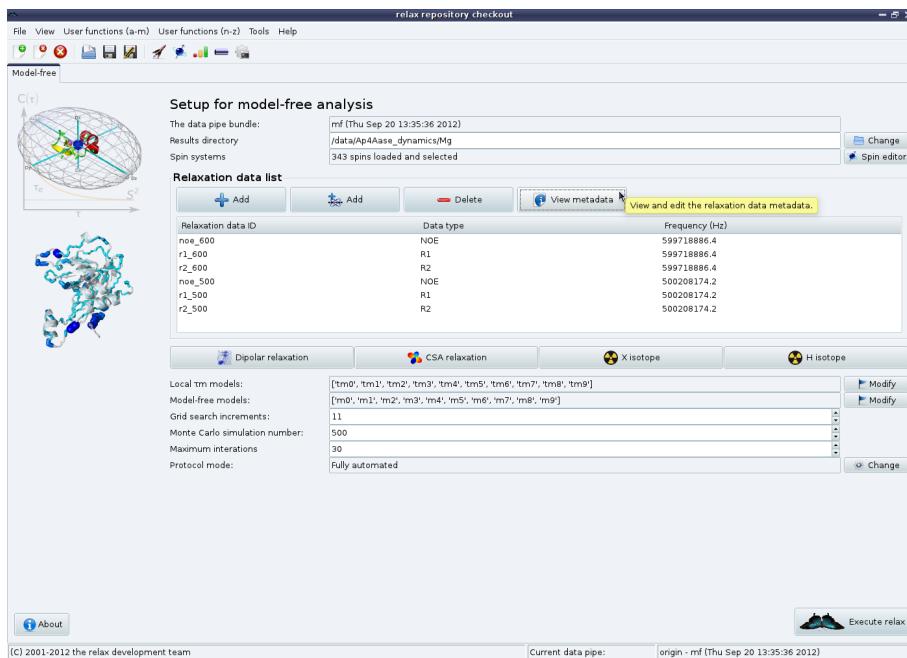
Then the temperature control method is given. For more details, please read the documentation provided in the wizard and see section 5.2.1 on page 50. Click on “Next” to continue.



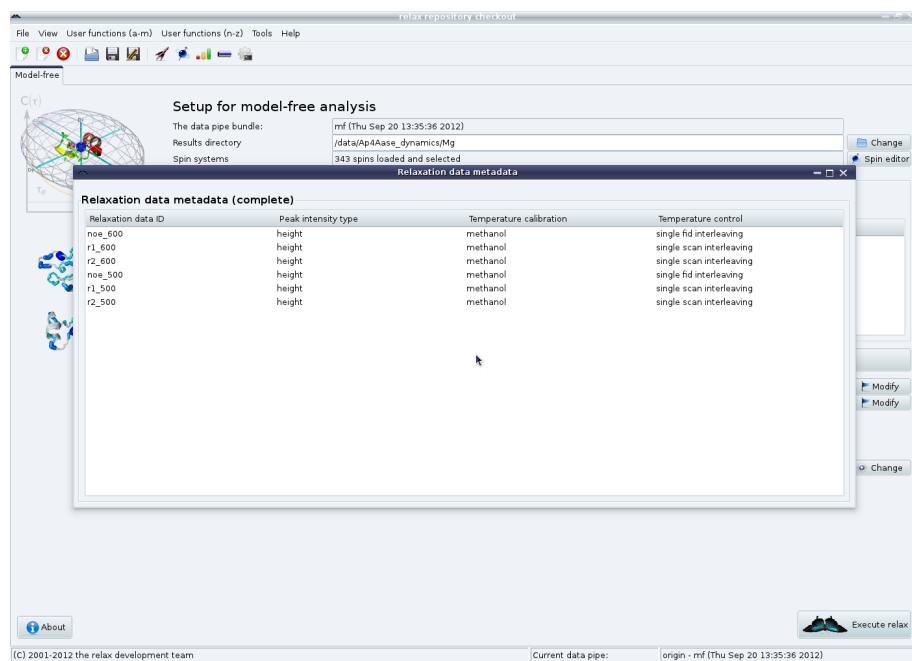
The temperature calibration method can finally be specified. Again, see section 5.2.1 on page 50 for the full details. Click on the “Finish” button to close the wizard.



After you have repeated this for the NOE, R₁ and R₂ at both 500 and 600 MHz, you should now see:

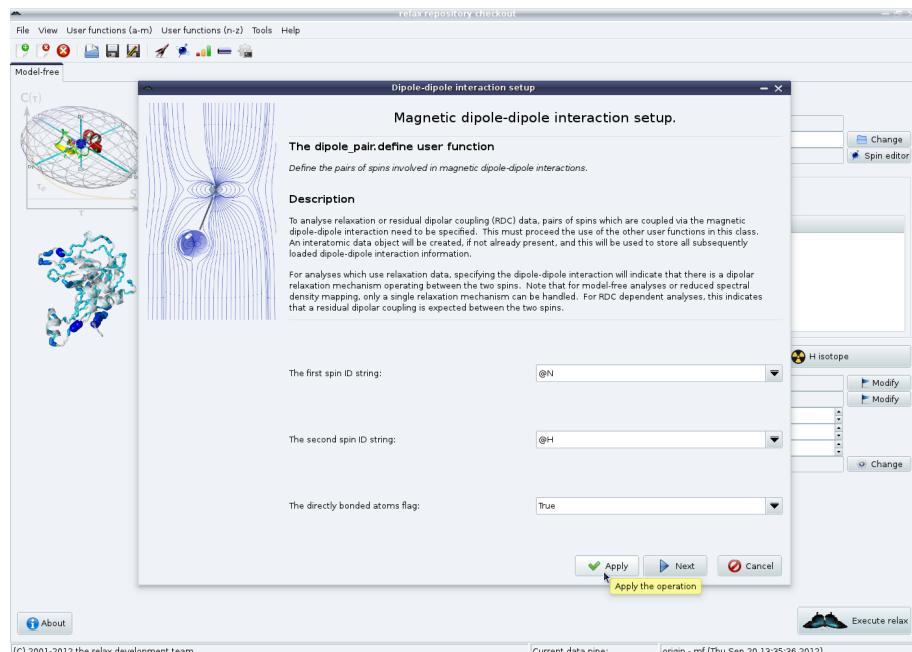


Check that the metadata has been properly entered by clicking on the “View metadata” button in the “Relaxation data list” GUI element:



7.9.6 d'Auvergne protocol GUI mode – relaxation interactions

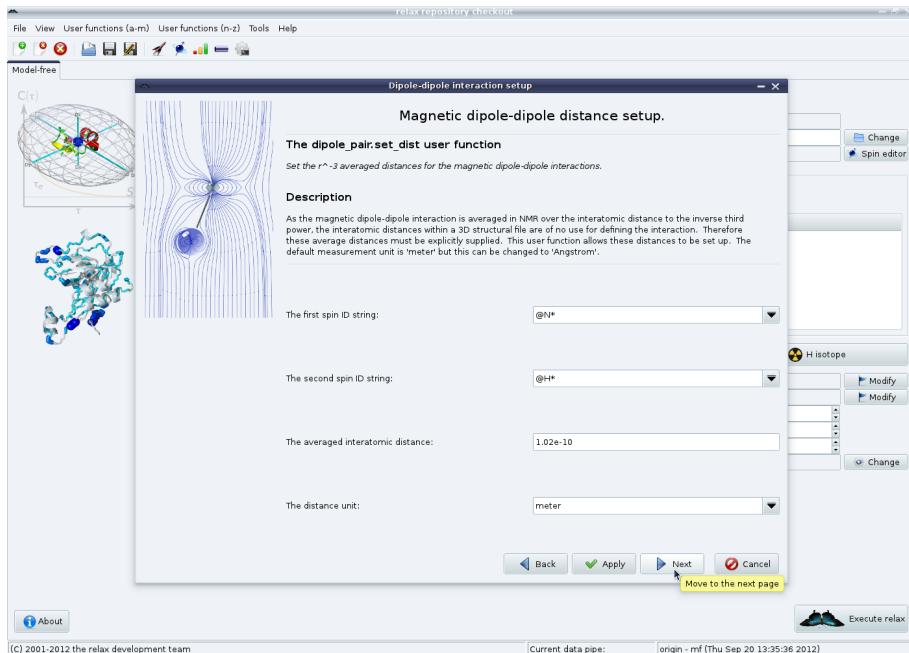
Just as in the scripting mode, the relaxation interactions need to now be defined. The first is the magnetic dipole-dipole interaction. All coupled nitrogen and proton spins should already be loaded at this point. Click on the “Dipolar relaxation” button in the model-free tab in the main relax window to launch the magnetic dipole-dipole interaction wizard:



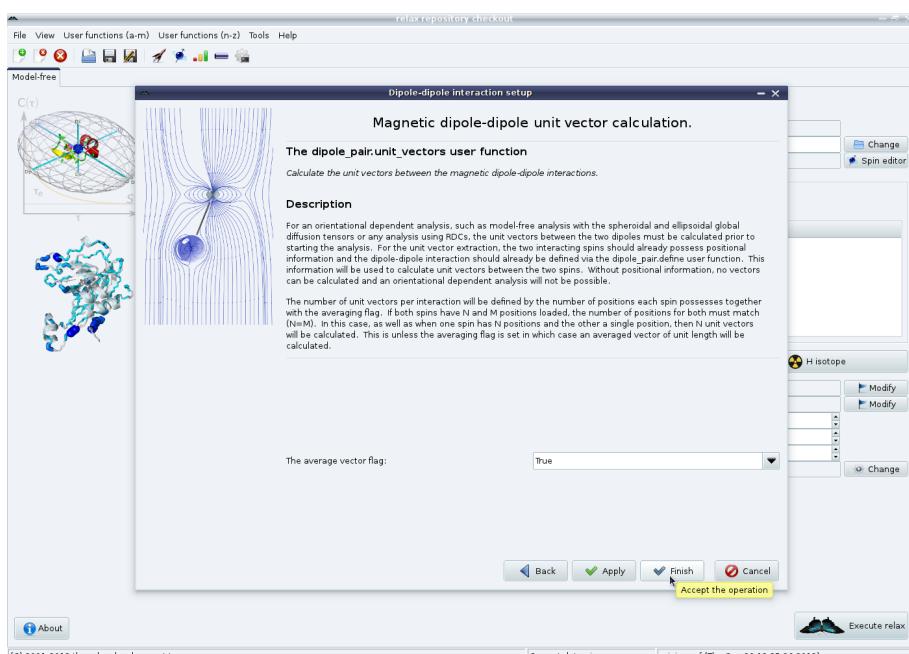
For this example, directly bonded nitrogens and protons will be analysed. To start with, the backbone NH pairs will be defined. Leave the values at “@N” and “@H” and click on the “Apply” button. Then change the two spin ID strings to “@NE1” and “@HE1” to set up the tryptophan sidechain indole NH pairs and click on the “Next” button. Note that

the regular expression “@N*” and “@H*” should not be used in this first wizard page as otherwise @N spins will be connected to @HE1 spins of the same tryptophan residue and @H spins to @NE1 spins.

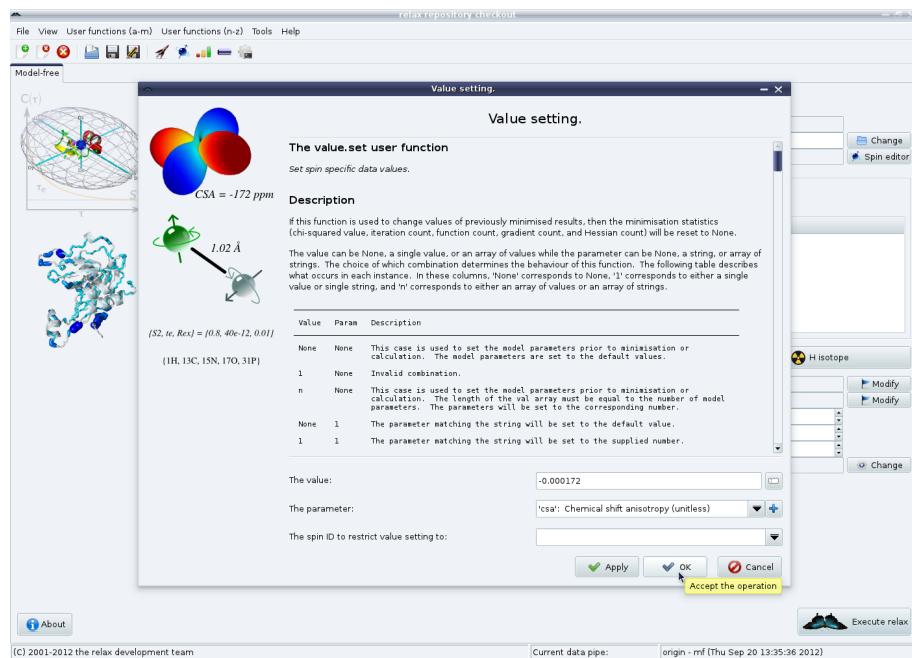
Now the $\langle r^{-3} \rangle$ averaged distance of 1.02 Å will be set. Leave all settings as they are and click on “Next”:



If multiple models have been loaded in the previous steps, then the unit vectors between each model need to be calculated. For a model-free analysis multiple unit vectors must be averaged to a single vector – current model-free theory is based on the assumption of a single vector orientation. Therefore the averaged vector flag must be left on “True”. Click on “Finish” to terminate the set up of the magnetic dipole-dipole interactions:

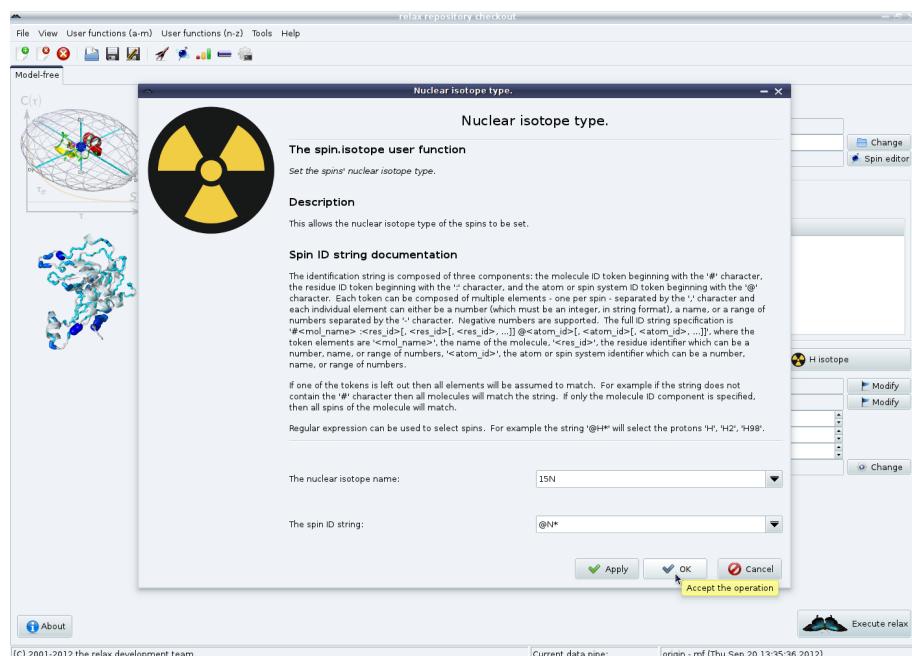


Secondly the chemical shift anisotropy (CSA) relaxation mechanism needs to be defined. Click on the “CSA relaxation” button in the model-free tab in the main relax window. An averaged CSA value of -172 ppm will be used for all spins, so simply click on “Ok” to finish.



7.9.7 d'Auvergne protocol GUI mode – spin isotopes

As the PDB file contains no isotope information, this needs to now be specified. First click on the “X isotope” button to set the nuclear isotope type of the heteronuclei:



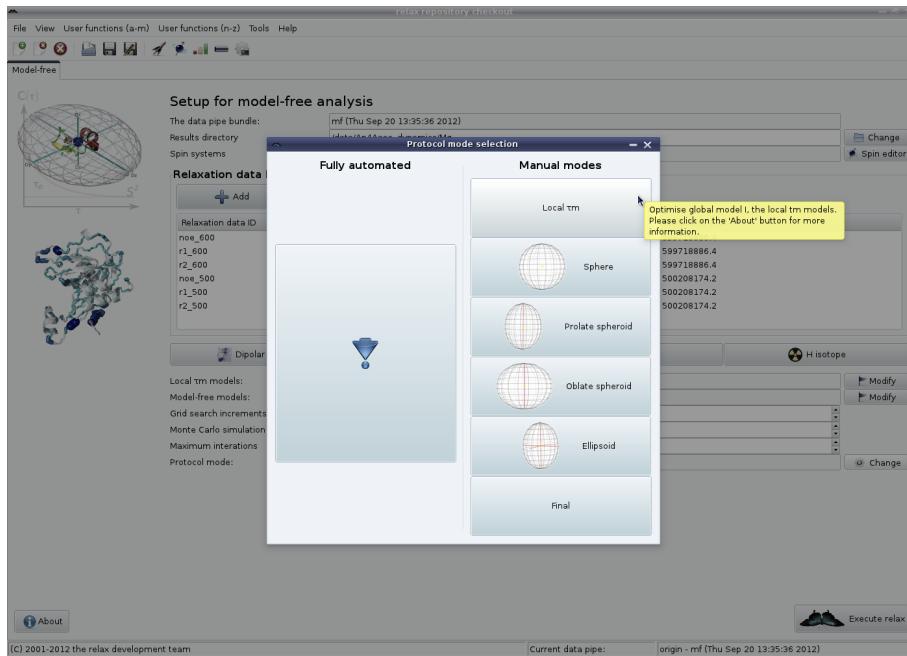
As nitrogen relaxation is being studied, the nuclear isotope name can be left as “15N” and the spin ID string to “@N*”. Therefore simply click on the “Ok” button. Exactly the same

procedure can be used for the proton with the “H isotope” button.

7.9.8 d'Auvergne protocol GUI mode – the rest of the setup

The local τ_m models and model-free models should not be modified, the reason for this is explained in section 7.8.2 on page 109. The grid search increments defaults to “11”. This is used in the optimisation of the individual model-free models for each spin. This value should also not be touched unless you know what you are doing (and have read d'Auvergne and Gooley (2008a)). The number of Monte Carlo simulations can be increased but, for accurate error estimates, it should not be less than 500 simulations. One additional setting is the “Maximum iterations”. This is a maximum number of times the protocol will iterate before terminating. This allows infinite loops to be broken. The value of 30 iterations should be fine for most analyses.

The “Protocol mode” GUI element setting of “Fully automated” will not be changed for the analysis of this tutorial. However if you are studying a system without a 3D structure, you can execute each individual component of the analysis by clicking on the “Change” button. This will make the protocol mode selection window appear:



From this you can first select the “Local τ_m ” model, then the “Sphere” and finally the “Final” mode, clicking on “Execute relax” between each selection.

7.9.9 d'Auvergne protocol GUI mode – execution

Prior to executing relax, you should very carefully check the relax controller window for any strange messages, warnings or errors. You can open this window in three ways:

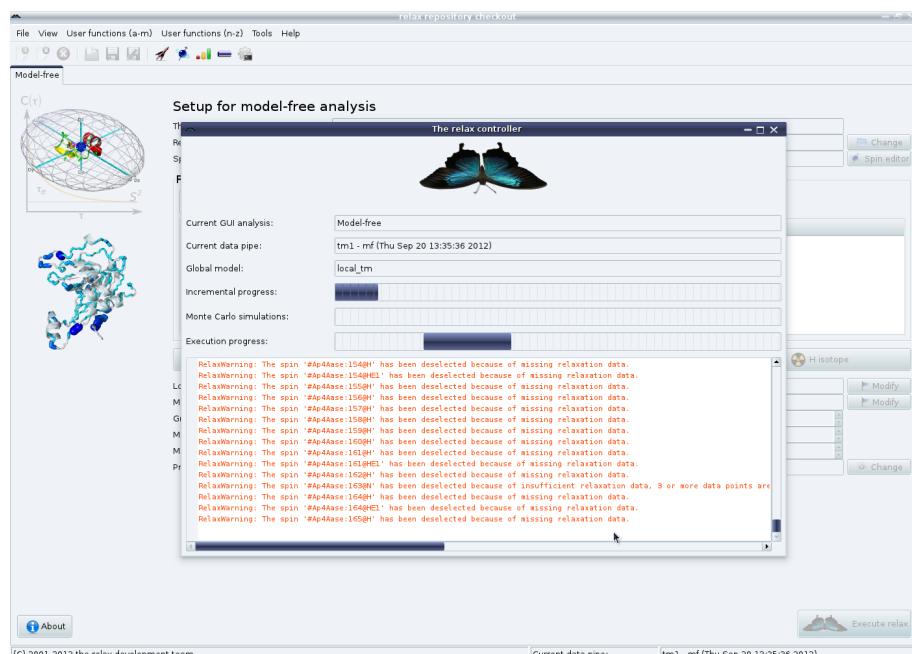
- Selecting the “View→Controller” menu item.

- Typing “[Ctrl+Z]” within the main relax window.
- Clicking on the “relax controller” button on the toolbar.

These messages are very important and will indicate to you if there are any problems prior to starting the very long model-free calculation. This information should be stored in the `log` file as well. As the execution of a fully iterative and complete model-free protocol takes a very long time to finish, it is advisable to save the current relax state. This will allow you restart the calculation without performing all of the steps detailed above. Just in case you cannot work out how to do this yourself, here is a list of the different ways you can do this (if this is not enough for you, please email the relax-users mailing list with your suggestions):

- Selecting the “File→Save relax state” menu item.
- Typing “[Ctrl+S]” within the main relax window.
- Clicking on the “Save relax state” button on the toolbar.
- Selecting the “File→Save as...” menu item.
- Typing “[Shift+Ctrl+S]” within the main relax window.
- Clicking on the “Save as” button on the toolbar.
- Selecting the “User functions→state→save” menu item.
- Opening up the relax prompt window with “View→relax prompt” or “[Ctrl+P]” and using the `state.save` user function.

If all the messages in the relax controller or `log` file appear to be fine and you have saved the current relax state, then click on “Execute relax”. This will start the calculations, freeze most of the GUI and open up the relax controller to give you feedback on the progress of the calculations:



At the start of the protocol, you should again check the messages carefully to be sure that relax is operating as you would expect. There may be very important **RelaxWarnings** that will require you to quit relax and start the analysis all over again.

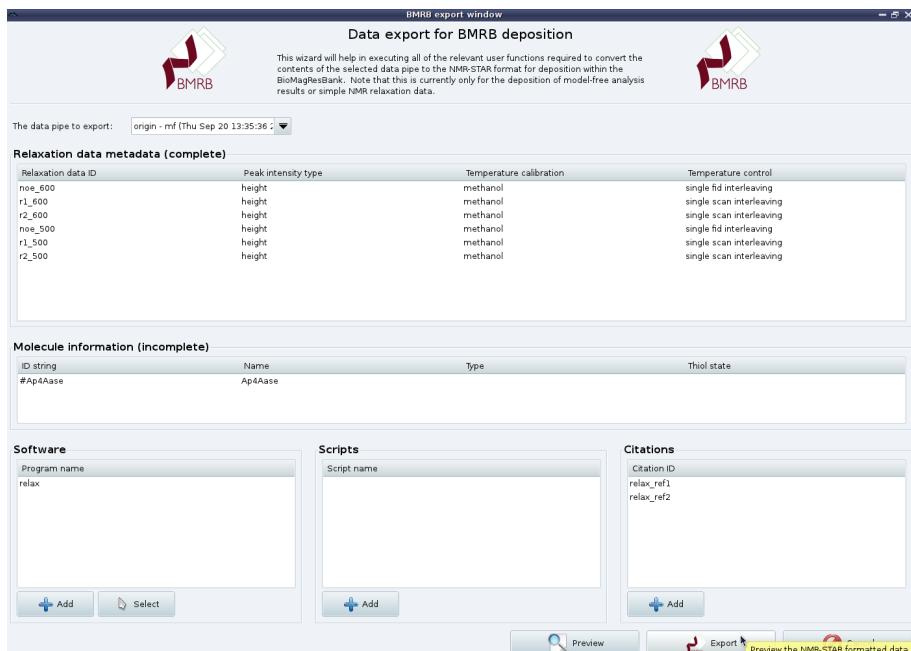
7.9.10 d'Auvergne protocol GUI mode – completion

Upon completion of the analysis, the save and results files for the final result will be located in the **final** directory within the selected results directory. The results files will consist of text files for each of the spin specific model-free parameters, 2D Grace plots of the model-free parameters, PyMOL and MOLMOL macros for superimposing the model-free parameter values onto the 3D structure of the molecule, and a PDB representation of the final diffusion tensor.

Further visualisations of the results are possible via the “User functions” menu entry. For example to generate a 2D plot of order parameters for one of the other diffusion tensor results, the pipe editor window can be used to switch data pipes to the other diffusion models and then the “User functions→grace→write” menu item can be selected to create the plot.

7.9.11 d'Auvergne protocol GUI mode – BMRB deposition

Once you are ready to publish your results, the very last step of the model-free analysis is to create a NMR-STAR formatted file for [BioMagResBank](#) submission for each model-free analysis you perform. This can be accomplished using the BMRB export window. Simply select the “File→Export for BMRB deposition” menu item. You will then see the BMRB export window:



From here you can complete the relaxation data metadata if needed, set up all the molecule information needed for a BMRB deposition, specify the software you have used running up

to the model-free analysis and any spectral processing or relax scripts you have used. You can also add as many citations relevant to your analysis as you wish. The NMR-STAR formatted file can be previewed in the relax controller window via the “Preview” button and the final file created using the “Export” button.

Once you are in the stage of writing up, simply go to the ADIT-NMR webpage at <http://deposit.bmrb.wisc.edu/bmrb-adit/>, create a new BMRB deposition, upload the file you have created, complete the deposition as needed, and add the BMRB deposition number to your paper.

Chapter 8

Reduced spectral density mapping

8.1 Introduction to reduced spectral density mapping

The reduced spectral density mapping analysis is often performed when the system under study is not suitable for model-free analysis, or as a last resort if a model-free analysis fails. The aim is to convert the relaxation data into three $J(\omega)$ values for the given field strength. Interpretation of this data, although slightly less convoluted than the relaxation data, is still plagued by problems related to non-spherical diffusion and much care must be taken when making conclusions. A full understanding of the model-free analysis and the effect of diffusion tensor anisotropy and rhombicity allows for better interpretation of the raw numbers.

To understand how reduced spectral density mapping is implemented in relax, the sample script will be worked through. This analysis type is not implemented in the GUI yet, though it shouldn't be too hard if anyone would like to contribute this and have a reference added to Chapter , the citations chapter.

8.2 $J(w)$ mapping script mode – the sample script

```
1 """Script for reduced spectral density mapping."""
2
3
4 # Create the data pipe.
5 pipe.create(pipe_name='my_protein', pipe_type='jw')
6
7 # Set up the 15N spins.
8 sequence.read(file='noe.600.out', res_num_col=1, res_name_col=2)
9 spin.name(name='N')
10 spin.element(element='N')
11 spin.isotope(isotope='15N', spin_id='@N')
12
13 # Load the 15N relaxation data.
14 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
15             res_num_col=1, data_col=3, error_col=4)
15 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
16             res_num_col=1, data_col=3, error_col=4)
```

```

16 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
17   res_num_col=1, data_col=3, error_col=4)
18
19 # Generate 1H spins for the magnetic dipole-dipole relaxation interaction.
20 sequence.attach_protons()
21
22 # Define the magnetic dipole-dipole relaxation interaction.
23 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
24 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)
25
26 # Define the chemical shift relaxation interaction.
27 value.set(val=-172 * 1e-6, param='csa')
28
29 # Select the frequency.
30 jw_mapping.set_frq(frq=600.0 * 1e6)
31
32 # Reduced spectral density mapping.
33 calc()
34
35 # Monte Carlo simulations (well, bootstrapping as this is a calculation and not a fit!).
36 monte_carlo.setup(number=500)
37 monte_carlo.create_data()
38 calc()
39 monte_carlo.error_analysis()
40
41 # Create grace files.
42 grace.write(y_data_type='j0', file='j0.agr', force=True)
43 grace.write(y_data_type='jwx', file='jwx.agr', force=True)
44 grace.write(y_data_type='jwh', file='jwh.agr', force=True)
45
46 # View the grace files.
47 grace.view(file='j0.agr')
48 grace.view(file='jwx.agr')
49 grace.view(file='jwh.agr')
50
51 # Write out the values.
52 value.write(param='j0', file='j0.txt', force=True)
53 value.write(param='jwx', file='jwx.txt', force=True)
54 value.write(param='jwh', file='jwh.txt', force=True)
55
56 # Finish.
57 results.write(file='results', force=True)
state.save('save', force=True)

```

8.3 J(w) mapping script mode – data pipe and spin system setup

The steps for setting up relax and the data model concept are described in full detail in Chapter 4. The first step, as for all analyses in relax, is to create a data pipe for storing all the data:

```

4 # Create the data pipe.
5 pipe.create(pipe_name='my_protein', pipe_type='jw')

```

Then, in this example, the ^{15}N spins are created from one of the NOE relaxation data files (Chapter 6):

```

7 # Set up the 15N spins.

```

```

8 sequence.read(file='noe.600.out', res_num_col=1, res_name_col=2)
9 spin.name(name='N')
10 spin.element(element='N')
11 spin.isotope(isotope='15N', spin_id='@N')

```

Skipping the relaxation data loading, the next part of the analysis is to create protons attached to the nitrogens for the magnetic dipole-dipole relaxation interaction:

```

18 # Generate 1H spins for the magnetic dipole-dipole relaxation interaction.
19 sequence.attach_protons()

```

This is needed to define the magnetic dipole-dipole interaction which governs relaxation.

8.4 J(w) mapping script mode – relaxation data loading

The loading of relaxation data is straight forward. This is performed prior to the creation of the proton spins so that the data is loaded only into the ^{15}N spin containers and not both spins for each residue. Only data for a single field strength can be loaded:

```

13 # Load the 15N relaxation data.
14 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
15     res_num_col=1, data_col=3, error_col=4)
15 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
16     res_num_col=1, data_col=3, error_col=4)
16 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
17     res_num_col=1, data_col=3, error_col=4)

```

The frequency of the data must also be explicitly specified:

```

28 # Select the frequency.
29 jw_mapping.set_frq(frq=600.0 * 1e6)

```

8.5 J(w) mapping script mode – relaxation interactions

Prior to calculating the $J(\omega)$ values, the physical interactions which govern relaxation of the spins must be defined. For the magnetic dipole-dipole relaxation interaction, the user functions are:

```

21 # Define the magnetic dipole-dipole relaxation interaction.
22 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
23 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)

```

For the chemical shift relaxation interaction, the user function call is:

```

25 # Define the chemical shift relaxation interaction.
26 value.set(val=-172 * 1e-6, param='csa')

```

8.6 J(w) mapping script mode – calculation and error propagation

Optimisation for this analysis is not needed as this is a direct calculation. Therefore the $J(\omega)$ values are simply calculated with the call:

```
31 # Reduced spectral density mapping.
32 calc()
```

The propagation of errors is more complicated. The Monte Carlo simulation framework of relax can be used to propagate the relaxation data errors to the spectral density errors. As this is a direct calculation, this collapses into the standard bootstrapping method. The normal Monte Carlo user functions can be called:

```
34 # Monte Carlo simulations (well, bootstrapping as this is a calculation and not a fit!).
35 monte_carlo.setup(number=500)
36 monte_carlo.create_data()
37 calc()
38 monte_carlo.error_analysis()
```

In this case, the `monte_carlo.initial_values` user function call is not required.

8.7 J(w) mapping script mode – visualisation and data output

The rest of the script is used to output the results to 2D Grace files for visualisation (the `grace.view` user function calls will launch Grace with the created files), and the output of the values into plain text files.

Chapter 9

Consistency testing

9.1 Introduction to the consistency testing of relaxation data

In spin relaxation, datasets are often recorded at different magnetic fields. This is especially important when R_2 values are to be used since μ s-ms motions contribute to R_2 . This contribution being scaled quadratically with the strength of the magnetic field, recording at multiple magnetic fields helps extract it. Also, acquiring data at multiple magnetic fields allows over-determination of the mathematical problems, e.g. in the model-free approach.

Recording at multiple magnetic fields is a good practice. However, it can cause artifacts if those different datasets are inconsistent. Inconsistencies can originate from, inter alia, the sample or the acquisition. Sample variations can be linked to changes in temperature, concentration, pH, etc. Water suppression is the main cause of acquisition variations as it affect relaxation parameters (especially NOE) of exposed and exchangeable moieties (e.g. the NH moiety).

It is thus a good idea to assess consistency of datasets acquired at different magnetic fields. For this purpose, three tests are implemented in relax. They are all based on the same principle – calculate a field independent value and compare it from one field to another.

The three tests are:

$J(0)$ The spectral density at the zero frequency calculated using the reduced spectral density approach.

F_η A consistency function proposed by [Fushman et al. \(1998\)](#).

F_{R_2} A consistency function proposed by [Fushman et al. \(1998\)](#).

These three tests are very similar (all probing consistency of R_2 data and all suffering from the same limitations) and any of them can be used for consistency testing. In the example below, the $J(0)$ values are used for consistency testing.

Different methods exist to compare tests values calculated from one field to another. These include correlation plots and histograms, and calculation of correlation, skewness and

kurtosis coefficients. The details of how to interpret such analyses are available at the end of this chapter in Section 9.7.

For more details on the tests and their implementation within relax, see:

- Morin, S. and Gagné, S. (2009a). Simple tests for the validation of multiple field spin relaxation data. *J. Biomol. NMR*, **45**, 361–372. ([10.1007/s10858-009-9381-4](https://doi.org/10.1007/s10858-009-9381-4))

Or for the origin of the tests themselves:

- Fushman, D., Tjandra, N., and Cowburn, D. (1999). An approach to direct determination of protein dynamics from ^{15}N NMR relaxation at multiple fields, independent of variable ^{15}N chemical shift anisotropy and chemical exchange contributions. *J. Am. Chem. Soc.*, **121**(37), 8577–8582. ([10.1021/ja9904991](https://doi.org/10.1021/ja9904991))

In addition, see the following review which includes a discussion on how to evaluate the reliability of recorded relaxation data:

- Morin, S. (2011). A practical guide to protein dynamics from ^{15}N spin relaxation in solution. *Prog. NMR Spectrosc.*, **59**(3), 245–262. ([10.1016/j.pnmrs.2010.12.003](https://doi.org/10.1016/j.pnmrs.2010.12.003))

9.2 Consistency testing in the prompt/script UI mode

The consistency testing analysis is only available via the prompt/script UI modes – no GUI auto-analysis has yet been built by a relax power-user.

9.2.1 Consistency testing script mode – the sample script

The following script can be found in the `sample_scripts` directory.

```
1 """ Script for consistency testing.
2
3 Severe artifacts can be introduced if model-free analysis is performed from inconsistent
4     multiple magnetic field datasets. The use of simple tests as validation tools for the
5     consistency assessment can help avoid such problems in order to extract more reliable
6     information from spin relaxation experiments. In particular, these tests are useful
7     for detecting inconsistencies arising from R2 data. Since such inconsistencies can
8     yield artificial Rex parameters within model-free analysis, these tests should be used
9     routinely prior to any analysis such as model-free calculations.
10
11 This script will allow one to calculate values for the three consistency tests J(0), F_eta
12     and F_R2. Once this is done, qualitative analysis can be performed by comparing
13     values obtained at different magnetic fields. Correlation plots and histograms are
14     useful tools for such comparison, such as presented in Morin & Gagne (2009a) J.
15     Biomol. NMR, 45: 361-372.
16
17
18 References
```

```

9 ======
10
11 The description of the consistency testing approach:
12
13 Morin & Gagne (2009a) Simple tests for the validation of multiple field spin
   relaxation data. J. Biomol. NMR, 45: 361-372. U{http://dx.doi.org/10.1007/s10858-009-9381-4}
14
15 The origins of the equations used in the approach:
16
17 J(0):
18   Farrow et al. (1995) Spectral density function mapping using 15N relaxation data
     exclusively. J. Biomol. NMR, 6: 153-162. U{http://dx.doi.org/10.1007/BF00211779}
19
20 F_eta:
21   Fushman et al. (1998) Direct measurement of 15N chemical shift anisotropy in
     solution. J. Am. Chem. Soc., 120: 10947-10952. U{http://dx.doi.org/10.1021/ja981686m}
22
23 F_R2:
24   Fushman et al. (1998) Direct measurement of 15N chemical shift anisotropy in
     solution. J. Am. Chem. Soc., 120: 10947-10952. U{http://dx.doi.org/10.1021/ja981686m}
25
26 A study where consistency tests were used:
27
28 Morin & Gagne (2009) NMR dynamics of PSE-4 beta-lactamase: An interplay of ps-ns order
   and us-ms motions in the active site. Biophys. J., 96: 4681-4691. U{http://dx.doi.org/10.1016/j.bpj.2009.02.068}
29 """
30
31 # Create the data pipe.
32 name = 'consistency'
33 pipe.create(name, 'ct')
34
35 # Set up the 15N spins.
36 sequence.read('noe.600.out', res_num_col=1)
37 spin.name(name='N')
38 spin.element(element='N')
39 spin.isotope(isotope='15N', spin_id='@N')
40
41 # Load the relaxation data.
42 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
   res_num_col=1, data_col=3, error_col=4)
43 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
   res_num_col=1, data_col=3, error_col=4)
44 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
   res_num_col=1, data_col=3, error_col=4)
45
46 # Generate the 1H spins for the magnetic dipole-dipole interaction.
47 sequence.attach_protons()
48
49 # Define the magnetic dipole-dipole relaxation interaction.
50 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
51 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)
52
53 # Define the chemical shift relaxation interaction.
54 value.set(val=-172 * 1e-6, param='csa')
55
56 # Set the angle between the 15N-1H vector and the principal axis of the 15N chemical shift
   tensor
57 value.set(val=15.7, param='orientation')
58

```

```

59 # Set the approximate correlation time.
60 value.set(val=13 * 1e-9, param='tc')
61
62 # Set the frequency.
63 consistency_tests.set_frq(frq=600.0 * 1e6)
64
65 # Consistency tests.
66 calc()
67
68 # Monte Carlo simulations.
69 monte_carlo.setup(number=500)
70 monte_carlo.create_data()
71 calc()
72 monte_carlo.error_analysis()
73
74 # Create grace files.
75 grace.write(y_data_type='j0', file='j0.agr', force=True)
76 grace.write(y_data_type='f_eta', file='f_eta.agr', force=True)
77 grace.write(y_data_type='f_r2', file='f_r2.agr', force=True)
78
79 # View the grace files.
80 grace.view(file='j0.agr')
81 grace.view(file='f_eta.agr')
82 grace.view(file='f_r2.agr')
83
84 # Finish.
85 results.write(file='results', force=True)
86 state.save('save', force=True)

```

This is similar in spirit to the reduced spectral density mapping sample script (Chapter 8 on page [127](#)).

9.3 Consistency testing script mode – data pipe and spin system setup

The steps for setting up relax and the data model concept are described in full detail in Chapter 4. The first step, as for all analyses in relax, is to create a data pipe for storing all the data:

```

31 # Create the data pipe.
32 name = 'consistency'
33 pipe.create(name, 'ct')

```

Then, in this example, the ^{15}N spins are created from one of the NOE relaxation data files (Chapter 6):

```

35 # Set up the  $^{15}\text{N}$  spins.
36 sequence.read('noe.600.out', res_num_col=1)
37 spin.name(name='N')
38 spin.element(element='N')
39 spin.isotope(isotope='15N', spin_id='@N')

```

Skipping the relaxation data loading, the next part of the analysis is to create protons attached to the nitrogens for the magnetic dipole-dipole relaxation interaction:

```

46 # Generate the 1H spins for the magnetic dipole-dipole interaction.
47 sequence.attach_protons()

```

This is needed to define the magnetic dipole-dipole interaction which governs relaxation.

9.4 Consistency testing script mode – relaxation data loading

The loading of relaxation data is straight forward. This is performed prior to the creation of the proton spins so that the data is loaded only into the ^{15}N spin containers and not both spins for each spin system. Note that if the relaxation data files contain spin information, then this order is not important. For this analysis, only data for a single field strength can be loaded:

```

41 # Load the relaxation data.
42 relax_data.read(ri_id='R1_600', ri_type='R1', frq=600.0*1e6, file='r1.600.out',
43     res_num_col=1, data_col=3, error_col=4)
43 relax_data.read(ri_id='R2_600', ri_type='R2', frq=600.0*1e6, file='r2.600.out',
44     res_num_col=1, data_col=3, error_col=4)
44 relax_data.read(ri_id='NOE_600', ri_type='NOE', frq=600.0*1e6, file='noe.600.out',
        res_num_col=1, data_col=3, error_col=4)

```

The frequency of the data must also be explicitly specified:

```

62 # Set the frequency.
63 consistency_tests.set_frq(frq=600.0 * 1e6)

```

9.5 Consistency testing script mode – relaxation interactions

Prior to calculating the $J(0)$, F_η , and F_{R_2} values, the physical interactions which govern relaxation of the spins must be defined. For the magnetic dipole-dipole relaxation interaction, the user functions are:

```

49 # Define the magnetic dipole-dipole relaxation interaction.
50 interatom.define(spin_id1='@N', spin_id2='@H', direct_bond=True)
51 interatom.set_dist(spin_id1='@N', spin_id2='@H', ave_dist=1.02 * 1e-10)

```

For the chemical shift relaxation interaction, the user function call is:

```

53 # Define the chemical shift relaxation interaction.
54 value.set(val=-172 * 1e-6, param='csa')

```

For the angle in degrees between the $^{15}\text{N}-^1\text{H}$ vector and the principal axis of the ^{15}N chemical shift tensor, the user function call is:

```

56 # Set the angle between the 15N-1H vector and the principal axis of the 15N chemical shift
      tensor
57 value.set(val=15.7, param='orientation')

```

9.6 Consistency testing script mode – calculation and error propagation

Optimisation for this analysis is not needed as this is a direct calculation. Therefore the $J(0)$, F_η , and F_{R_2} values are simply calculated with the call:

```
65 # Consistency tests.
66 calc()
```

The propagation of errors is more complicated. The Monte Carlo simulation framework of relax can be used to propagate the relaxation data errors to the spectral density errors. As this is a direct calculation, this collapses into the standard bootstrapping method. The normal Monte Carlo user functions can be called:

```
68 # Monte Carlo simulations.
69 monte_carlo.setup(number=500)
70 monte_carlo.create_data()
71 calc()
72 monte_carlo.error_analysis()
```

In this case, the `monte_carlo.initial_values` user function call is not required.

9.7 Consistency testing script mode – visualisation and data output

The rest of the script is used to output the results to 2D Grace files for visualisation (the `grace.view` user function calls will launch Grace with the created files), and the output of the values into plain text files.

However, simply visualizing the calculated $J(0)$, F_η , and F_{R_2} values this way does not allow proper consistency testing. Indeed, for assessing the consistency of relaxation data using these tests, different methods exist to compare values calculated from one field to another. These include correlation plots and histograms, and calculation of correlation, skewness and kurtosis coefficients.

To complete the consistency testing analysis, the following steps are needed:

- Extract the $J(0)$ values at multiple magnetic fields.
- Join together the data from a pair of magnetic fields either by pasting them as two columns of one file (approach A), or by dividing values from a first magnetic field by values from a second magnetic field (approach B).
- Make either a correlation plot (approach A), or an histogram of the ratios (approach B).
- See if the correlation plot is centered around a perfect correlation or skewed away (approach A), or if the values are centered around 1 in the histogram (approach B). If yes, data from multiple magnetic fields is consistent from one magnetic field to another. If no, data is inconsistent. In the case where inconsistency arises, if data

from more than two magnetic fields is available, more than one pair of data can be checked and the inconsistent magnetic field data can be identified.

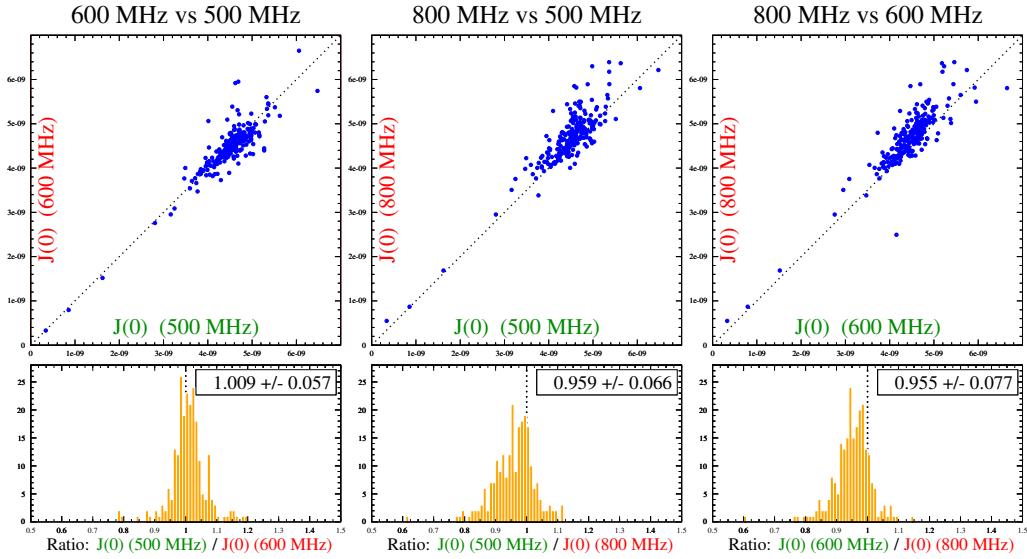


Figure 9.1: Example of consistency testing visual analysis. Relaxation data from three different magnetic fields are compared. For each pair of magnetic field, a correlation plot of the calculated $J(0)$ values (approach A, top) as well as an histogram of the ratio of calculated $J(0)$ values (approach B, bottom) are shown. These graphs must be manually created from the output of the sample script shown in section 9.2.1. The PSE-4 data, as published in [Morin and Gagné \(2009b\)](#), has been reused for the purpose of this example.

An example of such an analysis is shown in Figure 9.7. This example displays both consistent and inconsistent data. As the figure shows, the data recorded at 500 MHz and 600 MHz are consistent with each other whereas the data recorded at 800 MHz is consistent with the neither the 500 MHz nor 600 MHz data. Since more than two magnetic fields were used, this allowed the identification of the 800 MHz data as being inconsistent allowing the authors to take special care with this data set.

The 800 MHz data inconsistency is seen in the correlation plots (top) by a deviation from the dotted line (which represents the theoretical situation when equal $J(0)$ values are extracted from both magnetic fields). It is also observable in the histograms (bottom) where the ratio of the data from two magnetic fields is not centered at 1.0. In fact, there seems to be a systematic shift of the calculated $J(0)$ values at 800 MHz when compared to the two other magnetic fields. This is caused by a similar shift in the experimental R_2 (transversal relaxation rate) data.

For the 500 MHz and 600 MHz data pair, the data are centered around the dotted line in the correlation plot (approach A, top left) as well as centered around a value of 1.0 in the histogram comparing the ratios of values from both magnetic fields (approach B, bottom left). Of course, there are some outlier values even in the case of consistent data. There are caused by specific dynamic characteristics of these spins and are different from systematic inconsistencies such as depicted in the example above with the data recorded at 800 MHz.

Part III

Power users

Chapter 10

relax development

This chapter is for developers or those who would like to extend the functionality of relax. It is not required for using relax. If you would like to make modifications to the relax source code please subscribe to all the relax mailing lists (see the open source infrastructure chapter for more details). Announcements are sent to “relax-announce at gna.org” whereas “relax-users at gna.org” is the list where discussions about the usage of relax should be posted. “relax-devel at gna.org” is where all discussions about the development of relax including feature requests, program design, or any other discussions relating to relax’s structure or code should be posted. Finally, “relax-commits at gna.org” is where all changes to relax’s code and documentation, as well as changes to the web pages, are automatically sent to. Anyone interested in joining the project should subscribe to all four lists.

10.1 Version control using Subversion

The development of relax requires the use of the Subversion (SVN) version control software downloadable from <http://subversion.tigris.org/>. The source code to relax is stored in an SVN repository located at <http://svn.gna.org/svn/relax/>. Every single change which has ever made to the program is recorded within this repository. For more information see the open source infrastructure chapter 3 on page 29.

Although the downloadable distribution archives can be modified it is best that the most current and up to date revision (the *head* revision) is modified instead. More information about the basics of version control and how this is implemented in Subversion can be found in the Subversion book located at <http://svnbook.red-bean.com/>.

If you are not currently a relax developer you can check out the head revision by typing

```
$ svn co svn://svn.gna.org/svn/relax/trunk relax-trunk
```

Otherwise if you are a developer type

```
$ svn co svn+ssh://xxxxx@svn.gna.org/svn/relax/trunk relax-trunk
```

replacing `xxxxx` with your Gna! login name. If your version is out of date it can be updated to the latest revision by typing

```
$ svn up
```

Modifications can be made to these sources.

10.2 Coding conventions

The following conventions should be followed at all times for any code to be accepted into the relax repository. A Python script which tests if code meets relax's coding conventions is distributed with relax and is located at `scripts/code_validator`. The main reason for these conventions is for readability. By using a consistent coding style and a high comment ratio, the code becomes much easier to read for non-coders and those new to Python. It significantly decreases the barrier of entry into the relax source code for NMR spectroscopists.

10.2.1 Indentation

Indentation should be set to four spaces rather than a tab character. This is the recommendation given in the Python style guide found at <http://www.python.org/doc/essays/styleguide.html>. Emacs should automatically set the tabstop correctly. For vi add the following lines to the `vimrc` file:

```
set tabstop=4
set shiftwidth=4
set expandtab
```

For UNIX systems, including Linux and Mac OS X, the `vimrc` file is `~/.vimrc` whereas in MS Windows the file is `$VIM/_vimrc` which is usually `C:\Program Files\vim_vimrc`. Certain versions of vim, those within the 6.2 series, contain a bug where the tabstop value cannot be changed using the `vimrc` file (although typing “`:set tabstop=4`” in vim will fix it). One solution is to edit the file `python.vim` which on GNU/Linux systems is located in the path `/usr/share/vim/ftplugin/`. It contains the two lines

```
" Python always uses a 'tabstop' of 8.
setlocal ts=8
```

If these lines are deleted the bug will be removed. Another way to fix the problem is to install newer versions of the run-time files (which will do the same thing).

10.2.2 Doc strings

The following are relax's conventions for docstrings. Many of these are Python conventions.

- The standard Python convention of a one line description separated from a detailed description by an empty line should be adhered to. This line must start with a capital letter and end in a period. This convention is required for certain docstring parsers (see the Python docs).

- All functions should have a docstring describing in detail the function, structure, and organisation of the code.
- A docstring should be followed by an empty line.
- Indentation of the docstring should be the same as that of the first line of code, excluding indented lists, etc.

An example of a single line docstring is:

```
1 def delete(self):
2     """Function for deleting all model-free data."""
```

An example of a multiline docstring is:

```
1 def aic(chi2, k, n):
2     """Akaike's Information Criteria (AIC).
3
4     The formula is::
5
6         AIC = chi2 + 2k
7
8
9     @param chi2:    The minimised chi-squared value.
10    @type chi2:   float
11    @param k:      The number of parameters in the model.
12    @type k:      int
13    @param n:      The dimension of the relaxation data set.
14    @type n:      int
15    @return:       The AIC value.
16    @rtype:        float
17
18
19    return chi2 + 2.0*k
```

In addition to the text descriptions, the docstrings use the [Epydoc](#) markup language to describe arguments, return values, and other information about the code. See <http://epydoc.sourceforge.net/fields.html> for a listing of all the epydoc fields allowed. This mark up language is important for the creation of the [API documentation](#) and to help developers understand the purpose and operation of the code.

10.2.3 Variable, function, and class names

In relax a mixture of both camel case (eg. CamelCase) and lower case with underscores is used. Despite the variability there are fixed rules which should be adhered to. These naming conventions should be observed at all times.

Variables and functions

For both variables and functions lower case with underscores between words is always used. This is for readability as the convention is much more fluent than camel case. A few rare exceptions exist, an example is the Brownian diffusion tensor parameter of anisotropy \mathfrak{D}_a

which is referenced as `cdp.diff_tensor.Da`. As a rule though all new variable or function names should be kept as lower case. An example of this convention for both the variable name and function name is:

```

1  def assemble_param_vector(self, spin=None, spin_id=None, sim_index=None, model_type=
2      None):
3      """Assemble the model-free parameter vector (as numpy array).
4
5      If the spin argument is supplied, then the spin_id argument will be ignored.
6
7      @keyword spin:           The spin data container.
8      @type spin:             SpinContainer instance
9      @keyword spin_id:       The spin identification string.
10     @type spin_id:          str
11     @keyword sim_index:    The optional MC simulation index.
12     @type sim_index:       int
13     @keyword model_type:   The optional parameter set, one of 'all', 'diff', 'mf', or
14     'local_tm'.
15     @type model_type:      str or None
16
17     @return:                An array of the parameter values of the model-free model.
18     @rtype:                 numpy array
19
20
21     # Initialise.
22     param_vector = []
23
24
25     # Determine the model type.
26     if not model_type:
27         model_type = self.determine_param_set_type()
28
29     # Diffusion tensor parameters.
30     if model_type == 'diff' or model_type == 'all':
31         # Normal parameters.
32         if sim_index == None:
33             # Spherical diffusion.
34             if cdp.diff_tensor.type == 'sphere':
35                 param_vector.append(cdp.diff_tensor.tm)

```

Classes

For classes relax uses a mix of camel case (for example all the `RelaxError` objects) and underscores (for example `Model_free`). The first letter in all cases is always capitalised. Generally the camel case is reserved for very low level classes which are involved in the program's infrastructure. Examples include the `RelaxError` code, the threading code, and the relax data store code. All the data analysis specific code, generic code, interface code, etc. uses underscores between the words with only the first letter capitalised. One exception is the space mapping class `OpenDX`, the reason being that the program is called `OpenDX`. An example is:

```

1  class Model_free_main:
2      """Class containing functions specific to model-free analysis."""
3
4      def are_mf_params_set(self, spin):
5          """Test if the model-free parameter values are set.
6
7          @param spin:    The spin container object.
8          @type spin:    SpinContainer instance

```

```

9      @return:      The name of the first parameter in the parameter list in which the
10     corresponding parameter value is None. If all parameters are set, then None is
11     returned.
12
13     @rtype:       str or None
14
15     """
16
17     # Deselected residue.
18     if spin.select == 0:
19         return

```

Long names

If you have a look at a few relax source files, you will notice that the variable, function, and class names can be quite long. For example the model-free function `disassemble_param_vector()` and the RelaxError class `RelaxNoSequenceError`. While this is not normal for coding, it is an important component of relax as it facilitates the reading of the source code by a non-coder or someone not familiar with the codebase. Iteration counters can be single letter variables such as `i`, `j`, `k`, etc., however for all other variables, functions, and classes please attempt to use descriptive names which are instantly identifiable. Please minimise the amount of abbreviations used and only use those which are obvious. For example naming the parameter vector `self.param_vector`, the relaxation data `relax_data`, the model selection class `Model_selection`, the type of spheroidal diffusion `spheroid_type`, etc.

10.2.4 Whitespace

The following conventions are for general code cleanliness and readability:

- Trailing whitespace should be avoided, although this is not very important.
- All functions should be preceded by two empty lines. The only exception is the first function of the class definition.
- Function arguments should be separated by a comma followed by a single space.
- The assignment operator should be surrounded by spaces, for example `tm_=1e-8`. The exception is function arguments where for example `self.classic_colour(res_num=None, width=0.3)`.
- The comparison operators should also be surrounded by spaces, e.g. `<`, `>`, `==`, `<=`, `>=`, `<>`, `!=`, `is`, and `in`.

An example which shows most of these conventions is:

```

1  class Internal:
2      """The internal relax structural data object.
3
4      The structural data object for this class is a container possessing a number of
5      different arrays corresponding to different structural information. These objects are
6      described in the structural container docstring.
7
8      """

```

```

6
7     def _bonded_atom(self, attached_atom, index, mol):
8         """Find the atom named attached_atom directly bonded to the atom located at the
9             index.
10
11            @param attached_atom: The name of the attached atom to return.
12            @type attached_atom: str
13            @param index: The index of the atom which the attached atom is attached
14                to.
15            @type index: int
16            @param mol: The molecule container.
17            @type mol: MolContainer instance
18            @return: A tuple of information about the bonded atom.
19            @rtype: tuple consisting of the atom number (int), atom name (str)
20            , element name (str), and atomic position (Numeric array of len 3)
21            """
22
23
24     # Init.
25     bonded_found = False
26
27     # No bonded atoms, so determine the connectivities.
28     if not mol.bonded[index]:
29         # Determine the molecule type if needed.
30         if not hasattr(mol, 'type'):
31             self._mol_type(mol)

```

10.2.5 Comments

Comments are a very important component within relax. In the current source code the percentage of comment lines relative to lines of code ranges from 15% to over 30% for different files. The average comment density would be close to 25%. The purpose of having so many comment lines, much more than you would expect from source code, is so that the relax's code is fully self documented. It allows someone who is not familiar with the codebase to read the code and quickly understand what is happening. It simplifies the process of learning and allows NMR spectroscopists who are not coders to dive into the code. If writing code for relax, please attempt to maintain the tradition by aiming towards a 25% comment ratio. The comment should be descriptive of what the code below it is supposed to do. Most importantly the comment explains why that code exists. The script `scripts/code_validator` can be used to check the comment density.

10.3 Submitting changes to the relax project

10.3.1 Submitting changes as a patch

The preferred method for submitting fixes and improvements to the relax source code is by the creation of a patch. If your changes are a fix make sure you have submitted a bug report to the bug tracker located at <https://gna.org/bugs/?group=relax> first. See section 3.3 on page 30 for more details. Two methods can be used to generate the patch – the Unix command `diff` or the Subversion program. The resultant file `patch` of either the `diff` or `svn` command described below can be posted to the “relax-devel at gna.org”

mailing list. Please label within your post which version of relax you modified or which revision the patch is for. Also try to create a commit log message according to the format described in section 10.4.4 on page 148 for one of the relax committers to use as a template for committing the change.

10.3.2 Modification of official releases – creating patches with diff

If your modifications have been made to the source code of one of the official relax releases (for example 2.1.1) then the Unix command `diff` can be used to create a patch. A patch file is simply the output of the `diff` command run with the recursive flag and presented in the ‘unified’ format. Therefore two directories need to be compared. If the original sources are located in the directory `relax_orig` and the modified sources in `relax_mod` then the patch can be created by typing

```
$ diff -ur relax_orig relax_mod > patch
```

10.3.3 Modification of the latest sources – creating patches with Subversion

If possible changes to the latest sources is preferred. Using the most up to date sources from the relax SVN repository will significantly aid the relax developers to incorporate your changes back into the main development line. To check out the current development line see section 10.1 on page 141 for details. Prior to submitting a patch to the mailing list your sources should be updated to include the most recent changes. To do this type

```
$ svn up
```

and note the revision number to include in your post. The update may cause a conflict if changes added to the repository clash with your modifications. If this occurs see the Subversion book at <http://svnbook.red-bean.com/> for details on how to resolve the conflict or submit a message to the relax-devel list.

Once the sources are up to date your changes can be converted into the patch text file. Using SVN creating a patch is easy. Just type

```
$ svn diff > patch
```

in the base relax directory.

10.4 Committers

10.4.1 Becoming a committer

Anyone can become a relax developer and obtain commit access to the relax repository. The main criteria for selection by the relax developers is to show good judgement, competence in producing good patches, compliance with the coding and commit log conventions, comportment on the mailing lists, not producing too many bugs, only taking on challenges which can be handled, and the skill in judging your own abilities. You will also need to

have an understanding of the concepts of version control specifically those relating to Subversion. The SVN book at <http://svnbook.red-bean.com/> contains all the version control information you will need. After a number of patches have been submitted and accepted any of the relax developers can propose that you receive commit access. If a number of developers agree while no one says no then commit access will be offered.

One area where coding ability can be demonstrated is within the relax test suite. The addition of tests, especially those where the relax internal data structures of the relax data store are scrutinised, can be a good starting point for learning the structure of relax. This is because the introduction of bugs has no effect on normal program execution. The relax test suite is an ideal proving ground.

If skills in only certain areas of relax development, for example in creation of the documentation, an understanding of C but not python, an understanding of solely the code of the user interface, or an understanding of the code specific to a certain type of data analysis methodology, then partial commit access may be granted. Although you will have the ability to make modifications to any part of the repository please make modifications only those areas for which you have permission.

10.4.2 Joining Gna!

The first step in becoming a committer is to create a Gna! account. Go to <https://gna.org/account/register.php> and type in a login name, password, real name, and the email address you would like to use. You will then get an automatic email from Gna! which will contain a link to activate your registration.

10.4.3 Joining the relax project

The second step in becoming a committer is to register to become a member of the relax project. Go to the Gna! website (<https://gna.org/>) and login. Click on ‘My Groups’ to go to <https://gna.org/my/groups.php>. In the section ‘Request for inclusion’ type ‘relax’ and hit enter. Select relax and write something in the comments. If you have been approved (see section 10.4.1) you will be added to the project committers list.

10.4.4 Format of the commit logs

If you are a relax developer and you have commit access to the repository the following conventions should be followed for all commit messages.

- The length of all lines in the commit log should never exceed 100 characters. This is so that the log message viewed in either emails or by the command prompt command `svn log` is legible.
- The first line of the commit log should be a short description or synopsis of the changes. If the change relates to a bug or a task, include the bug and task number using the notation `type #num` where `type` is either `bug`, `task` or `support` and `num` is the id number (for example `bug #6503`). This terminology is important because the

Gna! infrastructure knows how to translate this into a link to the issue. Also include a link to the issue.

- The second line should be blank.
- If the commit is a bug fix reported by a non-committer or if the commit originates from a patch posted by a non-committer the next lines should be reserved for crediting. The name of the person and their obfuscated email address (for example edward_at_nmr-relax_dot_com) should be included in the message.
- Next should be another blank line.
- If the commit relates to an entry in the bug tracker or to a discussion on the mailing lists then the web address of either the bug report or the mailing list archive message should be cited in the next section (separated from the synopsis or credit section by a blank line). All relevant links should be included to allow easy navigation between the repository, mailing lists, bug tracker, etc. An example is bug #5559 which is located at https://gna.org/bugs/?func=detailitem&item_id=5559 and the post to “relax-devel at gna.org” describing the fix to that bug which is located at <https://mail.gna.org/public/relax-devel/2006-03/msg00013.html>.
- A full description with all the details can follow. This description should follow a blank line, can itself be sectioned using blank lines, and finally the log is terminated by one blank line at the end of the message.

An example of a commit message for the closure of a bug is:

`Fixing the rest of bug #7241 (https://gna.org/bugs/?7241).`

`Bug #7241 was thought to be fixed in r2591 and r2593, the commit messages describing the solution being located at https://mail.gna.org/public/relax-commits/2006-09/msg00064.html (Message-id: <E1GTgBi-0000R6-4h@subversion.gna.org>) for r2591 and https://mail.gna.org/public/relax-commits/2006-10/msg00001.html (Message-id: <E1GTTt6C-0005rk-8q@subversion.gna.org>) for r2593.`

`However this was not the only place that the Scientific Python PDB data structure peptide_chains was being accessed. The chains were being accessed in the file 'pipe_control/sequence.py' when the sequence was being read out of the PDB file. This has now been modified with changes similar to r2591 and r2593.`

An example of a commit message for changes relating to a task is:

`This change implements half of task #3630 (https://gna.org/task/?3630).`

`The docstring in the generic optimisation function has been modified to clear up the ambiguity cased by supplying the option 'None' together with Newton optimisation.`

One last commit message example is:

`Added the API documentation creation (using Epydoc) to the Scons scripts.`

`The Scons target to create the HTML API documentation is called 'api_manual.html'. The documentation can be created by typing: $ scons api_manual.html`

`The function 'compile_api_manual_html()' was added to the 'scons/manuals.py' file. This function runs the 'epydoc' command. All the Epydoc options are specified in that function.`

10.4.5 Discussing major changes

If you are contemplating major changes, either for a bug fix, to add a completely new feature or user function for your own work, to improve the behaviour of part the program, or any other potentially disruptive modifications, please discuss these ideas on the relax-devel mailing list. If the planned changes have the potential to introduce problems the creation of a private branch may be suggested.

10.5 Branches

10.5.1 Branch creation

If a change is likely to be disruptive or cause breakages in the program, the use of your own temporary branch is recommended. This private branch is a complete copy of one of the main development lines wherein you can make changes without disrupting the other developers. Although called a private branch every change is visible to all other developers and each commit will result in an automatic email to the relax-commits mailing list. Other developers are even able to check out your branch and make modifications to it. Private branches can also be used for testing ideas. If the idea does not work the branch can be deleted from the repository (in reality the branch will always exist between the revision numbers of its creation and deletion and can always be resurrected). For example to create a branch from the main development line, the ‘trunk’, called `molmol_macros` whereby new Molmol macros are to be written, type

```
$ svn cp svn+ssh://xxxxx@svn.gna.org/svn/relax/trunk \
svn+ssh://xxxxx@svn.gna.org/svn/relax/branches/molmol_macros
```

replacing `xxxxx` with your login name. You can then check out your private branch by typing

```
$ svn co svn+ssh://xxxxx@svn.gna.org/svn/relax/branches/molmol_macros
```

which will create a directory called `molmol_macros` containing all the relax source files. To have the files placed into a different directory, type the name of that directory at the end of the last command. Modifications can be made to this copy while normal development continues on the main line.

10.5.2 Keeping the branch up to date using `svnmerge.py`

As you develop your branch, changes will be occurring simultaneously within the main line. These changes should be merged into your branch on a regular basis to avoid large incompatible changes from forming between the two branches. To simplify this process, the `svnmerge.py` script located at <http://www.orcaware.com/svn/wiki/Svnmerge.py> can be used. It is best to download the trunk version from that page, unless that version is non-functional. Once you have this script, the merging from the main line to your private branch must be initialised by typing, from within the checked out copy of your branch,

```
$ svnmerge.py init
```

This then needs to be committed using the automatically generated log

```
$ svn ci -F svnmerge-commit-message.txt
```

To keep up to date, simply type

```
$ svnmerge.py merge
```

If conflicts have occurred please refer to the Subversion book at <http://svnbook.red-bean.com/> for information on how to resolve the problem. Otherwise, or once fixed, the main line revisions merged into your branch can be committed using the automatically generated log file:

```
$ svn ci -F svnmerge-commit-message.txt
```

10.5.3 Merging the branch back into the main line

Once you have completed the modifications desired for your branch, all changes which have occurred in the main line have been merged using `svnmerge.py`, and the changes have been approved for merging back into the main line – then your branch can be merged. First check out a copy of the main line,

```
$ svn co svn+ssh://xxxxx@svn.gna.org/svn/relax/trunk relax-trunk
```

or update a previously checked out version,

```
$ svn up
```

Then `svnmerge.py` can be utilised again. First initialise the merging process by typing, from within the checked out copy of the main line,

```
$ svnmerge.py init svn+ssh://xxxxx@svn.gna.org/svn/relax/branches/molmol_macros
```

Then commit the change

```
$ svn ci -F svnmerge-commit-message.txt
```

To merge the branch and commit the changes, type

```
$ svnmerge.py merge --bidirectional
```

```
$ svn ci -F svnmerge-commit-message.txt
```

Finally the merge properties need to be removed

```
$ svnmerge.py uninit -S svn+ssh://xxxxx@svn.gna.org/svn/relax/branches/molmol_macros
```

the changes committed

```
$ svn ci -F svnmerge-commit-message.txt
```

and your private branch deleted

```
$ svn rm svn+ssh://xxxxx@svn.gna.org/svn/relax/branches/molmol_macros
```

10.6 The SCons build system

The [SCons](#) build system was chosen over other build systems including `make` as it is a cross-platform build system which can be used in Unix, GNU/Linux, Mac OS X, and even MS Windows (the correct compilers are nevertheless required). Various components of the program relax can be created using the SCons utility. This includes C module compilation, manual creation, distribution creation, and cleaning up and removing certain files. The file `sconstruct` in the base relax directory, which consists of python code, directs the operation of SCons for the various functions.

10.6.1 SCons help

Multiple functions have been built into the `sconstruct` script and the modules of the `scons` directory. Each of these can be selected by specifying different “targets” when running SCons. A description of each target is given by the SCons help system which is accessible by typing `scons --help` in the base relax directory.

10.6.2 C module compilation

As described in the installation chapter, typing `scons` in the base directory will create the shared objects or dll files which are imported into Python as modules.

10.6.3 Compilation of the user manual (PDF version)

To create the PDF version of the relax user manual type

```
$ scons user_manual.pdf
```

in the base directory. SCons will then run a series of shell commands to create the manual from the L^AT_EX sources located in the `docs/latex` directory. This is dependent on the programs `latex`, `makeindex`, `dvips`, and `ps2pdf` being located within the environment’s path.

10.6.4 Compilation of the user manual (HTML version)

The HTML version of the relax user manual is made by typing

```
$ scons user_manual.html
```

in the base directory. One command calling the program `latex2html` will be executed which will create HTML pages from the L^AT_EX sources.

10.6.5 Compilation of the API documentation (HTML version)

The HTML version of the relax API documentation is made by typing

```
$ scons api_manual.html
```

in the base directory. The programs Epydoc and Graphviz are required for creating this documentation. The resultant HTML pages will be located in the directory `docs/api`.

10.6.6 Making distribution archives

Two types of distribution archive can be created from the currently checked out sources – the source and binary distributions. To create the source distribution type

```
$ scons source_dist
```

whereas to create the binary distribution, whereby the C modules are compiled and the resultant shared objects are included in the bzipped tar file, type

```
$ scons binary_dist
```

If a binary distribution does not exist for your architecture feel free to create it yourself and contribute the archive to be included on the download pages. To do this you will need to check out the appropriate tagged branch from the relax subversion repository. If the current stable release is called 1.2.3 check out that branch by typing

```
$ svn co svn+ssh://bugman@svn.gna.org/svn/relax/tags/1.2.3 relax
```

replacing `bugman` with your user name if you are a relax developer, otherwise typing

```
$ svn co svn://svn.gna.org/svn/relax/tags/1.2.3 relax
```

Then build the binary distribution and send a message to the relax development mailing list. If compilation does not work please submit a bug to the bug tracker system at <https://gna.org/bugs/?group=relax> detailing the relax version, operation system, architecture, and any other information you believe will help to solve the problem. More information about donating binary distributions to the relax project is given in the open source infrastructure chapter (Chapter 3, page 29).

10.6.7 Cleaning up

If the command

```
$ scons clean
```

is run in the base directory all Python byte compiled files `*.pyc`, all C object files `*.o` and `*.os`, and any backup files with the extension `*.bak` are removed from all sub-directories. In addition any temporary L^AT_EX compilation files are removed from the `docs/latex` directory.

The more powerful command

```
$ scons clean_all
```

will, in addition to all the files removed by the `clean` target, remove all compiled C shared object files (`*.so`, `*.dylib`, `*.pyd`) and the `build` and `dist` directories created when building the Mac OS X application.

10.7 The core design of relax

To enable flexibility the internal structure of relax is modular. By construction the large collection of independent data analysis tools can be used individually and relatively easily by any new code implementing other forms of relaxation data analysis or even by other programs. The core modular design of the program is shown in Figure 10.1.

10.7.1 The divisions of relax's source code

relax's source code can be divided into five major areas: the initialisation code, the user interface (UI) code, the functional code, the number crunching code, and the code storing the program state.

Initialisation: The code belonging to this section initialises the program, processes the command-line arguments, and determines what mode the program will be run in including the choice of the UI.

UI: The current UI modes in relax include the prompt, the script and the GUI modes. These consist of separate code paths, all sitting on top of the underlying functional code. In the future, a web-based interface may be added.

Functional code: This code is the main part of the program. It includes anything which does not fit into the other sections and comprises the generic code, the specific code, and the specific setup code used as an interface between the two.

Number crunching: The computationally expensive code belongs in this section.

Program state: The state of the program is contained within the relax data store which is accessible from all parts of the program as a singleton object.

10.7.2 The major components of relax

Each of the boxes in Figure 10.1 represents a different grouping of code.

relax: The top level module. This initialises the entire program, tests the dependencies, sets up the multi-processor framework and specific processor fabric, and prints the program's introduction message.

Command line arguments: This code processes the arguments supplied to the program and decides whether to print the help message, initialise the prompt, execute a script, initialise a different UI, run the program in test mode, or run the program as a slave thread.

Prompt: The main user interface consisting of a Python prompt. The namespace of the interpreter contains the various user functions which are front ends to the generic code. The user functions are simply Python functions which test the supplied arguments to make sure they are of the correct type (string, integer, list, or any other type) before sending the values to the generic code. The code for the prompt is located in the directory `prompt/`.

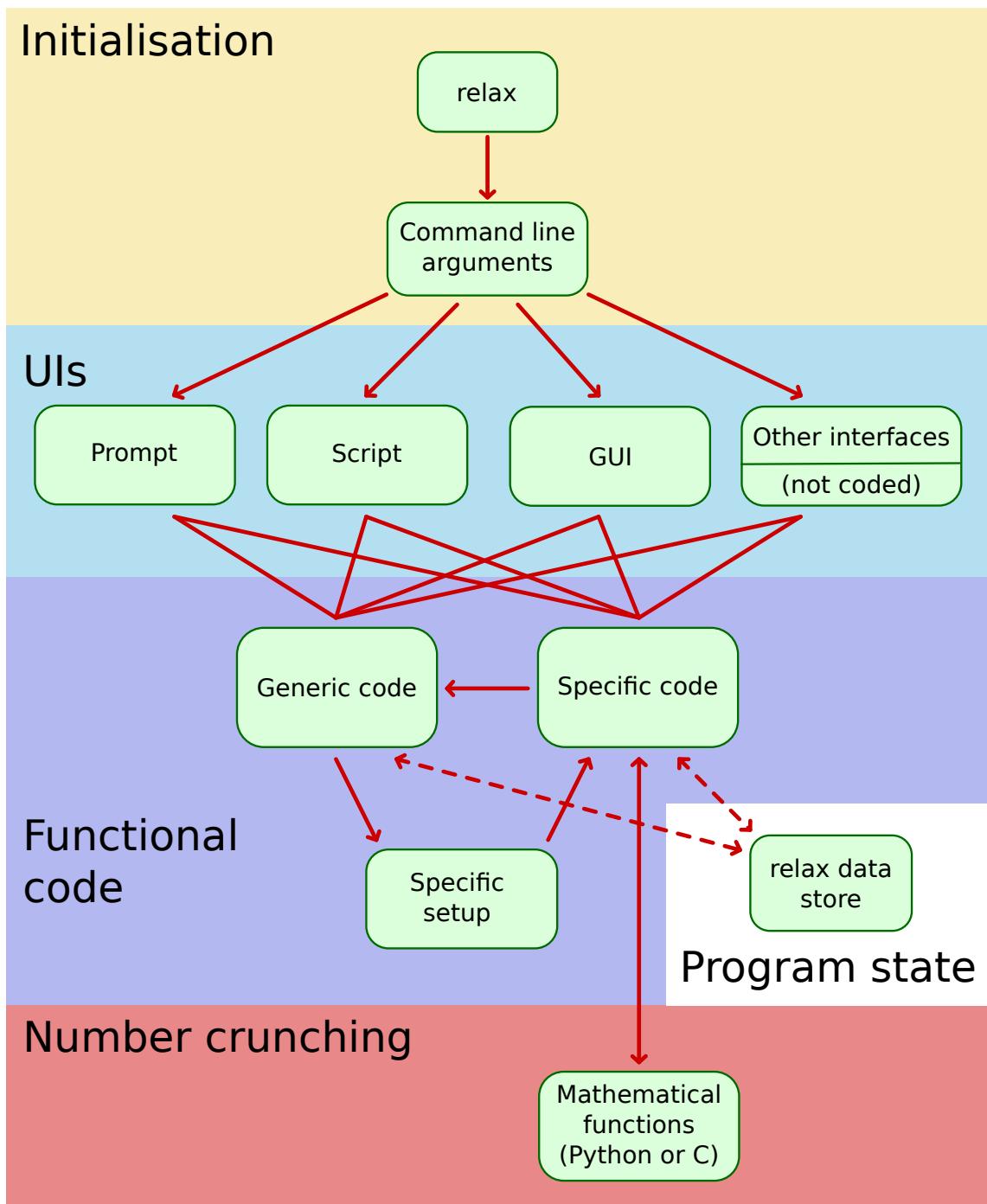


Figure 10.1: The core design of relax.

Script: If a script is supplied on the command line or executed within another user interface it will be run in the same namespace as that of the prompt. Hence the script has access to all the user functions available at the relax prompt. This allows commands which are typed at the prompt to be pasted directly and unmodified into a text file to be run as a script.

GUI: The graphical user interface code base is located in the `gui` directory.

Other interfaces: Any number of interfaces (for example a web-based interface or an ncurses interface) could be added to relax without modification of the current sources. This must be, without question, developed within the relax source code repository otherwise the code will not be maintainable in the future and will be almost impossible back into relax later on.

Generic code: This code includes classes and functions which are independent of the UI and not specific to a certain data pipe type, for example not being involved in model-free analysis, relaxation curve-fitting, the NOE calculation, and reduced spectral density mapping. All this code is located in the directory `pipe_control/`.

Specific setup: This code implements the internal interface between the generic and specific code. The generic code calls the specific setup asking for a specific function for the given data pipe type. For example by asking for the `minimise` function when the data pipe type is model-free analysis the model-free specific `minimise()` method is returned. Although the generic code accesses the specific code solely through this interface the specific code can access the generic code directly. The code is located in the file `specific_fns/specific_setup.py`.

Specific code: This is the code which is specific to the data pipe type – model-free analysis, relaxation curve-fitting, reduced spectral density mapping, and the NOE calculation. Each type is located in a separate file in the directory `specific_fns/`.

Mathematical functions: This is reserved for CPU intensive code involved in calculations. The code may be written in Python however C code can be used to significantly increase the speed of the calculations. For optimisation the code can include function evaluations, calculation of gradients, and calculation of Hessians. These functions are located in the directory `maths_fns/`.

Data: The program state stored in the relax data store singleton object. This class contains all the program data and is accessed by the generic and specific code. The mathematical functions may also access this data but this is not recommended. The structure is initialised by the file `data/__init__.py`.

10.8 The mailing lists for development

10.8.1 Private vs. public messages

If you would like to start a private discussion, please label your email as such. Private messages are however strongly discouraged, only start a private conversation if you really must.

If you receive a reply to a message you have sent, a bug report you have filed, etc. which has not been sent to the mailing list and has not been labelled as private, then the most likely explanation is that “reply-to-all” has not been used and hence the mailing list has not been included on the CC list. If this occurs, please ask the person if the message was meant to be private and refrain from discussing any of the comments within the post. Save these comments until after the person responds by saying that the message was private or re-sends the message to the mailing list. Try to encourage public messages if you think that the post need not be private and if you think that it would be useful for the mailing list archives.

For thread consistency, if you send a message which accidentally misses the mailing list, please do not then forward the previously sent message to the list. For better readability of the mailing list archives, it is best that you create an entirely new message responding to the original post. Just cut and paste your miss-directed message into your new message. That way the thread will be continuous – there will not be any messages missing from the middle of the thread in between the original post and your forwarded message.

To simplify the process of checking if the message was supposed to be private, you could copy-and-paste the following message (modifying it as you see fit):

Sorry in advance, but the following is the standard pre-composed response to a post not sent to the relax mailing lists and not labelled as private. If you would like to start a private conversation about relax, please label your message as such. If you really must start a private exchange, please respond to this message saying so. If your message was meant to be sent to the relax mailing list, please send the message again. For this, please copy-and-paste your message, replying to the original (i.e. no forwarding), and making sure that the mailing list is in the CC field by clicking on “reply-to-all”.

10.9 The bug, task, and support request trackers

relax’s infrastructure includes three different issue trackers. These are the [bug tracker](#), the [task tracker](#), and the [support request tracker](#).

10.9.1 Submitting a bug report

If someone reports a bug to one of the relax mailing lists, ask that person if they would like to create a bug report for that problem, pointing them to the submission web page. This is a good starting point to allow the person to become more involved in the relax project. If they do not respond or say that they would prefer not to, then you can create bug report for the issue linking to the original message and crediting the person for reporting the issue.

10.9.2 Assigning an issue to yourself

If you are a relax committer and see an issue which you would like to solve, please assign that issue to yourself before you start work on it. The assignment will prevent duplicated

efforts. If you can see an area where relax needs work, feel free to create a report within task tracker and then assign the task to yourself.

10.9.3 Closing an issue

When closing an issue (whether a bug report, a task, or a support request) a number of steps need to be taken. The tracker status should be changed to “Done” and the issue “Closed”. In addition, a message should be included which states the repository revision and the relax-commits mailing list archive link (with the message-id) in which the issue was solved. If multiple commits were required, then include all the revisions and as many links as possible (if a task required many commits, the relax-commits links could be skipped). An example is [bug #7402](#) where the closing comment was:

```
This documentation bug was fixed in r2641. The commit message is located at  
https://mail.gna.org/public/relax-commits/2006-10/msg00073.html (Message-id:  
<E1GYG41-0002kK-Jx@subversion.gna.org>).
```

10.10 Links, links, and more links

Creating links throughout the relax infrastructure is important for two major reasons – navigation and search engine indexing. When including a link to a post within the mailing list archives, please include the message-id email header. This enables subscribers to the mailing lists to search for the specific message within their local copy of the email messages.

10.10.1 Navigation

To be able to easily navigate between the relax infrastructure components – the bug tracker, the task tracker, the support request tracker, the relax-devel mailing list, the commit logs, and the SVN and CVS repositories – try to include as many links as possible.

For example a bug may first be reported on the relax-users mailing list, then placed within the bug tracker, discussed on relax-devel, a fix committed to the repository, and finally the bug report closed. To be able to follow this chain, links are very important (email message-ids are also important). When the bug is first added to the bug tracker, a link to the relax-users mailing list archive message and the message-id should be included. If you start a discussion on relax-devel, try to include links to the bug tracker entry and the relax-users message. When committing a fix to the repository, include links to the bug report, to the start of the thread in the mailing list archive, and the original message to relax-users. Then when the bug report is closed, include the revision number of the fix and a link to the relax-commits archive message (and message-id). By having all these links, it is then very easy for someone else to jump between the systems and follow the progression of the bug fix.

If you send a message referring to an old post which was sent to the relax mailing lists, an old bug report, or any other archived information, please take the time to find that original information in the archives and include a link to it (including the message-id if relevant).

It is much more efficient for a single person to hunt down that message than for the many recipients of your post to search for the message themselves. By including the link, you decrease the overhead of following the mailing list.

10.10.2 Search engine indexing

Having a large web of links across relax's infrastructure aids in the search engine indexing of the mailing list archives and the <http://www.nmr-relax.com> web site. The web of links is useful for catching those Google bots. That way the Google searching of the mailing list archives located on the [communication web page](#) will be more up to date. However to increase the search engine ranking of the web site, links to <http://www.nmr-relax.com> from external sites is required. This is one reason why relax can be found at a number of sites across the web:

Freecode: New relax releases are announced not only on the [relax-announce](#) mailing list and on the relax [news](#) pages, but also on [Freecode](#). This used to be called Freshmeat.

The mail archive: This site archives all of the relax mailing lists, including [relax-announce](#), [relax-users](#), [relax-devel](#), and [relax-commits](#).

Gmane: Pronounced as "main", the relax mailing lists are also archived at Gmane in numerous formats. The archived relax mailing lists include [relax-announce](#) ([thread](#), [blog](#), [NNTP](#), [RSS](#)), [relax-users](#) ([thread](#), [blog](#), [NNTP](#), [RSS](#)), [relax-devel](#) ([thread](#), [blog](#), [NNTP](#), [RSS](#)), and [relax-commits](#) ([thread](#), [blog](#), [NNTP](#), [RSS](#)).

MARC - Mailing list ARChives: This site archives all of the relax mailing lists, including [relax-announce](#), [relax-users](#), [relax-devel](#), and [relax-commits](#).

CIA.vc: This is the open source version control informant. CIA tracks open source projects in real-time. The relax real-time open source activity stats page is <http://cia.vc/stats/project/relax>. This website also has pages for each of the relax developers (in alphabetical order): [Edward d'Auvergne](#), [Michael Bieri](#), [Chris MacRaild](#), [Sébastien Morin](#), [Andrew Perry](#), [Han Sun](#), [Gary Thompson](#).

LinuxLinks.com: LinuxLinks.com, the Linux portal, is a website listing many Linux software projects. relax can be found on the [Software:Scientific:Biology:Proteins](#) page.

Softpedia: This is the encyclopedia of free software downloads. The relax page on Softpedia is <http://linux.softpedia.com/get/Science/relax-22351.shtml>. The relax developers pages are: [Edward d'Auvergne](#).

Pro-Linux: Diese ist eine der größten deutschsprachigen Seiten zum Thema Linux. The relax page is <http://www.pro-linux.de/cgi-bin/DBApp/check.cgi?ShowApp..10010.100>.

Part IV

Advanced topics

Chapter 11

Optimisation

11.1 Implementation

11.1.1 The interface

Optimisation or minimisation is available in relax via the `grid_search` and `minimise` user functions. The mathematical model optimised depends on the current data pipe type – it is implemented differently for each specific analysis. For analyses such as the steady state NOE (Chapter 6) or reduced spectral density mapping (Chapter 8), the solution can be found by direct calculation rather than optimisation. In these cases, the `calc` user function should be used instead.

11.1.2 The minfx package

To minimise target functions within relax, the minfx optimisation library is used (<https://gna.org/projects/minfx/>). This Python package is bundled with the official relax distribution archives. If you are using a version of relax checked out directly from the source code repository, you will need to manually install minfx as a standard Python package.

The minfx library originated as one of relax’s packages, but has been spun off as its own project for the benefit of other scientific, analytical, or numerical projects. Minfx is complete, very stable, well tested. Numerous optimisation algorithms are supported and can be clustered into three major categories – the line search methods, the trust-region methods, and the conjugate gradient methods.

The supported line search methods include:

- Steepest descent,
- Back-and-forth coordinate descent,
- Quasi-Newton BFGS,
- Newton,

- Newton-CG.

The supported trust-region methods include:

- Cauchy point,
- Dogleg,
- CG-Steihaug,
- Exact trust region.

The supported conjugate gradient methods include:

- Fletcher-Reeves,
- Polak-Ribière,
- Polak-Ribière +,
- Hestenes-Stiefel.

In addition, the following miscellaneous algorithms are implemented:

- Grid search,
- Nelder-Mead simplex,
- Levenberg-Marquardt.

The step selection subalgorithms include:

- Backtracking line search,
- Nocedal and Wright interpolation based line search,
- Nocedal and Wright line search for the Wolfe conditions,
- More and Thuente line search,
- No line search.

The Hessian modification subalgorithms include:

- Unmodified Hessian,
- Eigenvalue modification,
- Cholesky with added multiple of the identity,
- The Gill, Murray, and Wright modified Cholesky algorithm,

- The Schnabel and Eskow 1999 algorithm.

All methods can be constrained by:

- The Method of Multipliers (also known as the Augmented Lagrangian),
- The logarithmic barrier function.

These lists may be out of date, so please see the minfx website for additional information.

11.2 The optimisation space

The optimisation of the parameters of an arbitrary model is dependent on a function f which takes the current parameter values $\theta \in \mathbb{R}^n$ and returns a single real value $f(\theta) \in \mathbb{R}$ corresponding to position θ in the n -dimensional space. For it is that single value which is minimised as

$$\hat{\theta} = \arg \min_{\theta} f(\theta), \quad (11.1)$$

where $\hat{\theta}$ is the parameter vector which is equal to the argument which minimises the function $f(\theta)$. In most analyses in relax, $f(\theta)$ is the chi-squared equation

$$\chi^2(\theta) = \sum_{i=1}^n \frac{(y_i - y_i(\theta))^2}{\sigma_i^2}, \quad (11.2)$$

where i is the summation index over all data, y_i is the experimental data, $y_i(\theta)$ is the back calculated data, and σ_i is the experimental error.

11.3 Topology of the space

The problem of finding the minimum is complicated by the fact that optimisation algorithms are blind to the curvature of the complete space. Instead they rely on topological information about the current and, sometimes, the previous parameter positions in the space. The techniques use this information to walk iteratively downhill to the minimum.

11.3.1 The function value

At the simplest level all minimisation techniques require at least a function which will supply a single value for different parameter values θ . Conceptually this is the height of the space at the current position. For certain algorithms, such a simplex minimisation, this single value suffices.

11.3.2 The gradient

Most techniques also utilise the gradient at the current position. Although symbolically complex in the case of model-free analysis, for example, the gradient can simply be calculated as the vector of first partial derivatives of the chi-squared equation with respect to each parameter. It is defined as

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial \theta_1} \\ \frac{\partial}{\partial \theta_2} \\ \vdots \\ \frac{\partial}{\partial \theta_n} \end{pmatrix} \quad (11.3)$$

where n is the total number of parameters in the model.

The gradient is supplied as a second function to the algorithm which is then utilised in diverse ways by different optimisation techniques. The function value together with the gradient can be combined to construct a linear or planar description of the space at the current parameter position by first-order Taylor series approximation

$$f(\theta_k + x) \approx f_k + x^T \nabla f_k, \quad (11.4)$$

where f_k is the function value at the current parameter position θ_k , ∇f_k is the gradient at the same position, and x is an arbitrary vector. By accumulating information from previous parameter positions a more comprehensive geometric description of the curvature of the space can be exploited by the algorithm for more efficient optimisation.

An example of a powerful algorithm which requires both the value and gradient at current parameter values is the BFGS quasi-Newton minimisation. The gradient is also essential for the use of the Method of Multipliers constraints algorithm (also known as the Augmented Lagrangian algorithm).

11.3.3 The Hessian

The best and most comprehensive description of the space is given by the quadratic approximation of the topology which is generated from the combination of the function value, the gradient, and the Hessian. From the second-order Taylor series expansion the quadratic model of the space is

$$f(\theta_k + x) \approx f_k + x^T \nabla f_k + \frac{1}{2} x^T \nabla^2 f_k x, \quad (11.5)$$

where $\nabla^2 f_k$ is the Hessian, which is the symmetric matrix of second partial derivatives of the function, at the position θ_k . The Hessian is the matrix of second partial derivatives and is defined as

$$\nabla^2 = \begin{pmatrix} \frac{\partial^2}{\partial \theta_1^2} & \frac{\partial^2}{\partial \theta_1 \cdot \partial \theta_2} & \cdots & \frac{\partial^2}{\partial \theta_1 \cdot \partial \theta_n} \\ \frac{\partial^2}{\partial \theta_2 \cdot \partial \theta_1} & \frac{\partial^2}{\partial \theta_2^2} & \cdots & \frac{\partial^2}{\partial \theta_2 \cdot \partial \theta_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2}{\partial \theta_n \cdot \partial \theta_1} & \frac{\partial^2}{\partial \theta_n \cdot \partial \theta_2} & \cdots & \frac{\partial^2}{\partial \theta_n^2} \end{pmatrix}. \quad (11.6)$$

The order in which the partial derivatives are calculated is inconsequential, hence the Hessian is symmetric.

As the Hessian is computationally expensive a number of optimisation algorithms try to approximate it, the BFGS algorithm being a notable example. The most powerful minimisation algorithm for model-free analysis – Newton optimisation – requires the value, gradient, and Hessian at the current parameter values.

11.4 Optimisation algorithms

Prior to minimisation, all optimisation algorithms require a starting position within the optimisation space. This initial parameter vector is found by employing a coarse grid search – chi-squared values at regular positions spanning the space are calculated and the grid point with the lowest value becomes the starting position. The grid search itself is an optimisation technique. As it is computationally expensive the number of grid points needs to be kept to a minimum. Hence the initial parameter values are a rough and imprecise approximation of the local minimum.

Once the starting position has been determined by the grid search the optimisation algorithm can be executed. The number of algorithms developed within the mathematical field of optimisation is considerable. They can nevertheless be grouped into one of a small number of major categories based on the fundamental principles of the technique. These include the line search methods, the trust region methods, and the conjugate gradient methods. For more details on the algorithms described below see [Nocedal and Wright \(1999\)](#).

11.4.1 Line search methods

The defining characteristic of a line search algorithm is to choose a search direction p_k and then to find the minimum along that vector starting from θ_k ([Nocedal and Wright, 1999](#)). The distance travelled along p_k is the step length α_k and the parameter values for the next iteration are

$$\theta_{k+1} = \theta_k + \alpha_k p_k. \quad (11.7)$$

The line search algorithm determines the search direction p_k whereas the value of α_k is found using an auxiliary step-length selection algorithm.

The steepest descent algorithm

One of the simplest line search methods is the steepest descent algorithm. The search direction is simply the negative gradient, $p_k = -\nabla f_k$, and hence the direction of maximal descent is always followed. This method is inefficient – the linear rate of convergence requires many iterations of the algorithm to reach the minimum and it is susceptible to being trapped on saddle points within the space.

The coordinate descent algorithm

The coordinate descent algorithms are a simplistic group of line search methods whereby the search directions alternate between vectors parallel to the parameter axes. For the back-and-forth coordinate descent the search directions cycle in one direction and then back again. For example for a three parameter model the search directions cycle $\theta_1, \theta_2, \theta_3, \theta_2, \theta_1, \theta_2, \dots$, which means that each parameter of the model is optimised one by one. The method becomes less efficient when approaching the minimum as the step length α_k continually decreases (ibid.).

The BFGS algorithm

The quasi-Newton methods begin with an initial guess of the Hessian and update it at each iteration using the function value and gradient. Therefore the benefits of using the quadratic model of (11.5) are obtained without calculating the computationally expensive Hessian. The Hessian approximation B_k is updated using various formulae, the most common being the BFGS formula (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970). The search direction is given by the equation $p_k = -B_k^{-1}\nabla f_k$. The quasi-Newton algorithms can attain a superlinear rate of convergence, being superior to the steepest descent or coordinate descent methods.

The Newton algorithm

The most powerful line search method when close to the minimum is the Newton search direction

$$p_k = -\nabla^2 f_k^{-1} \nabla f_k. \quad (11.8)$$

This direction is obtained from the derivative of (11.5) which is assumed to be zero at the minimum of the quadratic model. The vector p_k points from the current position to the exact minimum of the quadratic model of the space. The rate of convergence is quadratic, being superior to both linear and superlinear convergence. The technique is computationally expensive due to the calculation of the Hessian. It is also susceptible to failure when optimisation commences from distant positions in the space as the Hessian may not be positive definite and hence not convex, a condition required for the search direction both to point downhill and to be reasonably oriented. In these cases the quadratic model is a poor description of the space. This algorithm is also known as the Newton-Raphson method.

The Newton conjugate gradient algorithm

A practical Newton algorithm which is robust for distant starting points is the Newton conjugate gradient method (Newton-CG). This line search method, which is also called the truncated Newton algorithm, finds an approximate solution to Equation (11.8) by using a conjugate gradient (CG) sub-algorithm. Retaining the performance of the pure Newton algorithm, the CG sub-algorithm guarantees that the search direction is always downhill as the method terminates when negative curvature is encountered.

The auxiliary step-length selection algorithm

Once the search direction has been determined by the above algorithms the minimum along that direction needs to be determined. Not to be confused with the methodology for determining the search direction p_k , the line search itself is performed by an auxiliary step-length selection algorithm to find the value α_k . A number of step-length selection methods can be used to find a minimum along the line $\theta_k + \alpha_k p_k$. One is the backtracking line search of Nocedal and Wright (1999). This method is inexact – it takes a starting step length α_k and decreases the value until a sufficient decrease in the function is found. Another is the line search method of Moré and Thuente (1994). Designed to be robust, the MT algorithm finds the exact minimum along the search direction and guarantees sufficient decrease.

11.4.2 Trust region methods

In the trust region class of algorithms the curvature of the space is modelled quadratically by (11.5). This model is assumed to be reliable only within a region of trust defined by the inequality $\|p\| \leq \Delta_k$ where p is the step taken by the algorithm and Δ_k is the radius of the n -dimensional sphere of trust (Nocedal and Wright, 1999). The solution sought for each iteration of the algorithm is

$$\min_{p \in \mathbb{R}^n} m_k(p) = f_k + p^T \nabla f_k + \frac{1}{2} p^T B_k p, \quad \text{s.t. } \|p\| \leq \Delta_k, \quad (11.9)$$

where $m_k(p)$ is the quadratic model, B_k is a positive definite matrix which can be the true Hessian as in the Newton model or an approximation such as the BFGS matrix, and $\|p\|$ is the Euclidean norm of p . The trust region radius Δ_k is modified dynamically during optimisation – if the quadratic model is found to be a poor representation of the space the radius is decreased whereas if the quadratic model is found to be reasonable the radius is increased to allow larger, more efficient steps to be taken.

The Cauchy point algorithm

The Cauchy point algorithm is similar in concept to the steepest descent line search algorithm. The Cauchy point is the point lying on the gradient which minimises the quadratic model subject to the step being within the trust region. By iteratively finding the Cauchy point the local minimum can be found. The convergence of the technique is inefficient, being similar to that of the steepest descent algorithm.

The dogleg algorithm

In changing the trust region radius the exact solutions to (11.9) map out a curved trajectory which starts parallel to the gradient for small radii. The end of the trajectory, which occurs for radii greater than the step length, is the bottom of the quadratic model. The dogleg algorithm attempts to follow a similar path by first finding the minimum along the gradient and then finding the minimum along a trajectory from the current point to the bottom

of the quadratic model. The minimum along the second path is either the trust region boundary or the quadratic solution. The matrix B_k of (11.9) can be the BFGS matrix, the unmodified Hessian, or a Hessian modified to be positive definite.

Steihaug's algorithm

Another trust region algorithm is Steihaug's modified conjugate gradient approach ([Steihaug, 1983](#)). For each step k an iterative technique is used which is almost identical to the standard conjugate gradient procedure except for two additional termination conditions. The first is if the next step is outside the trust region, the second is if a direction of zero or negative curvature is encountered.

The exact trust region

An almost exact solution to (11.9) can be found using an algorithm described in [Nocedal and Wright \(1999\)](#). This exact trust region algorithm aims to precisely find the minimum of the quadratic model m_k of the space within the trust region Δ_k . Any matrix B_k can be used to construct the quadratic model. However, the technique is computationally expensive.

11.4.3 Conjugate gradient methods

The conjugate gradient algorithm (CG) was originally designed as a mathematical technique for solving a large system of linear equations [Hestenes and Stiefel \(1952\)](#), but was later adapted to solving nonlinear optimisation problems ([Fletcher and Reeves, 1964](#)). The technique loops over a set of directions p_0, p_1, \dots, p_n which are all conjugate to the Hessian ([Nocedal and Wright, 1999](#)), a property defined as

$$p_i^T \nabla^2 f_k p_j = 0, \quad \text{for all } i \neq j. \quad (11.10)$$

By performing line searches over all directions p_j the solution to the quadratic model (11.5) of the position θ_k will be found in n or less iterations of the CG algorithm where n is the total number of parameters in the model. The technique performs well on large problems with many parameters as no matrices are calculated or stored. The algorithms perform better than the steepest descent method and preconditioning of the system is used to improve optimisation. Preconditioned techniques include the Fletcher-Reeves algorithm which was the original conjugate gradient optimisation technique ([Fletcher and Reeves, 1964](#)), the Polak-Ribière method ([Polak and Ribi  re, 1969](#)), a modified Polak-Ribière method called the Polak-Ribière + method ([Nocedal and Wright, 1999](#)), and the Hestenes-Stiefel algorithm which originates from a formula in [Hestenes and Stiefel \(1952\)](#). As a line search is performed to find the minimum along each conjugate direction both the backtracking and Mor   and Thuente auxiliary step-length selection algorithms will be tested with the CG algorithms.

11.4.4 Hessian modifications

The Newton search direction, used in both the line search and trust region methods, is dependent on the Hessian being positive definite for the quadratic model to be convex so that the search direction points sufficiently downhill. This is not always the case as saddle points and other non-quadratic features of the space can be problematic. Two classes of algorithms can be used to handle this situation. The first involves using the conjugate gradient method as a sub-algorithm for solving the Newton problem for the step k . The Newton-CG line search algorithm described above is one such example. The second class involves modifying the Hessian prior to, or at the same time as, finding the Newton step to guarantee that the replacement matrix B_k is positive definite. The convexity of B_k is ensured by its eigenvalues all being positive.

The first modification uses the Cholesky factorisation of the matrix B_k , initialised to the true Hessian, to test for convexity (Algorithm 6.3 of [Nocedal and Wright \(1999\)](#)). If factorisation fails the matrix is not positive definite and a constant τ_k times the identity matrix I is then added to B_k . The constant originates from the Robbins norm of the Hessian $\|\nabla^2 f_k\|_F$ and is steadily increased until the factorisation is successful. The resultant Cholesky lower triangular matrix L can then be used to find the approximate Newton direction. If τ_k is too large the convergence of this technique can approach that of the steepest descent algorithm.

The second method is the Gill, Murray, and Wright (GMW) algorithm ([Gill et al., 1981](#)) which modifies the Hessian during the execution of the Cholesky factorisation $\nabla^2 f_k = L D L^T$, where L is a lower triangular matrix and D is a diagonal matrix. Only a single factorisation is required. As rows and columns are interchanged during the algorithm the technique may be slow for large problems such as the optimisation of the model-free parameters of all spins together with the diffusion tensor parameters. The rate of convergence of the technique is quadratic.

11.4.5 Other methods

Nelder-Mead simplex

Some optimisation algorithms cannot be classified within line search, trust region, or conjugate gradient categories. For example the well known Nelder-Mead simplex optimisation algorithm. The technique is often used as the only the function value is employed and hence the derivation of the gradient and Hessian can be avoided. The simplex is created as an n -dimensional geometric object with $n + 1$ vertices. The first vertex is the starting position. Each of the other n vertices are created by shifting the starting position by a small amount parallel to one of unit vectors defining the coordinate system of the space. Four simple rules are used to move the simplex through the space: reflection, extension, contraction, and a shrinkage of the entire simplex. The result of these movements is that the simplex moves in an amoeboid-like fashion downhill, shrinking to pass through tight gaps and expanding to quickly move through non-convoluted space, eventually finding the minimum.

Key to these four movements is the pivot point, the centre of the face created by the n vertices with the lowest function values. The first movement is a reflection – the vertex

with the greatest function value is reflected through the pivot point on the opposite face of the simplex. If the function value at this new position is less than all others the simplex is allowed to extend – the point is moved along the line to twice the distance between the current position and the pivot point. Otherwise if the function value is greater than the second highest value but less than the highest value, the reflected simplex is contracted. The reflected point is moved to be closer to the simplex, its position being half way between the reflected position and the pivot point. Otherwise if the function value at the reflected point is greater than all other vertices, then the original simplex is contracted – the highest vertex is moved to a position half way between the current position and the pivot point. Finally if none of these four movements yield an improvement, then the simplex is shrunk halfway towards the vertex with the lowest function value.

Levenberg-Marquardt algorithm

Another algorithm is the commonly used Levenberg-Marquardt algorithm ([Levenberg, 1944](#); [Marquardt, 1963](#)). This is the algorithm used by the model-free analysis programs Modelfree4, Dasha, and Tensor2. This technique is designed for least-squares problems to which the chi-squared equation (11.2) belongs. The key to the algorithm is the replacement of the Hessian with the Levenberg-Marquardt matrix $J^T J + \lambda I$, where J is the Jacobian of the system calculated as the matrix of partial derivatives of the residuals, $\lambda > 0$ is a factor related to the trust-region radius, and I is the identity matrix. The algorithm is conceptually allied to the trust region methods and its performance varies finely between that of the steepest descent and the pure Newton step. When far from the minimum λ is large and the algorithm takes steps close to the gradient; when in vicinity of the minimum λ heads towards zero and the steps taken approximate the Newton direction. Hence the algorithm avoids the problems of the Newton algorithm when non-convex curvature is encountered and approximates the Newton step in convex regions of the space.

The technique does have one weak point though which is often mentioned only in the small print. That is that the algorithm catastrophically fails when the Levenberg-Marquardt matrix is singular. This occurs whenever a parameter is undefined. For example in a model-free analysis if the order parameter is one, then the corresponding internal correlation time can take any value. Performing a grid search with such undefined points greatly amplifies the problem and is the reason why many published model-free papers contain results with order parameters fixed at one ([d'Auvergne and Gooley, 2008a](#)).

11.5 Constraint algorithms

To guarantee that the minimum will still be reached the implementation of constraints limiting the parameter values together with optimisation algorithms is not a triviality. For this to occur the space and its boundaries must remain smooth thereby allowing the algorithm to move along the boundary to either find the minimum along the limit or to slide along the limit and then move back into the centre of the constrained space once the curvature allows it.

11.5.1 Method of Multipliers algorithm

One of the most powerful approaches is the Method of Multipliers ([Nocedal and Wright, 1999](#)), also known as the Augmented Lagrangian. Instead of a single optimisation the algorithm is iterative with each iteration consisting of an independent unconstrained minimisation on a sequentially modified space. When inside the limits the function value is unchanged but when outside a penalty, which is proportional to the distance outside the limit, is added to the function value. This penalty, which is based on the Lagrange multipliers, is smooth and hence the gradient and Hessian are continuous at and beyond the constraints. For each iteration of the Method of Multipliers the penalty is increased until it becomes impossible for the parameter vector to be in violation of the limits. This approach allows the parameter vector θ outside the limits yet the successive iterations ensure that the final results will not be in violation of the constraint.

For inequality constraints, each iteration of the Method of Multipliers attempts to solve the quadratic sub-problem

$$\min_{\theta} \mathcal{L}_A(\theta, \lambda^k; \mu_k) \stackrel{\text{def}}{=} f(\theta) + \sum_{i \in \mathfrak{I}} \Psi(c_i(\theta), \lambda_i^k; \mu_k), \quad (11.11)$$

where the function Ψ is defined as

$$\Psi(c_i(\theta), \lambda^k; \mu_k) = \begin{cases} -\lambda^k c_i(\theta) + \frac{1}{2\mu_k} c_i^2(\theta) & \text{if } c_i(\theta) - \mu_k \lambda^k \leq 0, \\ -\frac{\mu_k}{2} (\lambda^k)^2 & \text{otherwise.} \end{cases} \quad (11.12)$$

In (11.11), θ is the parameter vector; \mathcal{L}_A is the Augmented Lagrangian function; k is the current iteration of the Method of Multipliers; λ^k are the Lagrange multipliers which are positive factors such that, at the minimum $\hat{\theta}$, $\nabla f(\hat{\theta}) = \lambda_i \nabla c_i(\hat{\theta})$; $\mu_k > 0$ is the penalty parameter which decreases to zero as $k \rightarrow \infty$; \mathfrak{I} is the set of inequality constraints; and $c_i(\theta)$ is an individual constraint value. The Lagrange multipliers are updated using the formula

$$\lambda_i^{k+1} = \max(\lambda_i^k - c_i(\theta)/\mu_k, 0), \quad \text{for all } i \in \mathfrak{I}. \quad (11.13)$$

The gradient of the Augmented Lagrangian is

$$\nabla \mathcal{L}_A(\theta, \lambda^k; \mu_k) = \nabla f(\theta) - \sum_{i \in \mathfrak{I} | c_i(\theta) \leq \mu_k \lambda_i^k} \left(\lambda_i^k - \frac{c_i(\theta)}{\mu_k} \right) \nabla c_i(\theta), \quad (11.14)$$

and the Hessian is

$$\nabla^2 \mathcal{L}_A(\theta, \lambda^k; \mu_k) = \nabla^2 f(\theta) + \sum_{i \in \mathfrak{I} | c_i(\theta) \leq \mu_k \lambda_i^k} \left[\frac{1}{\mu_k} \nabla c_i^2(\theta) - \left(\lambda_i^k - \frac{c_i(\theta)}{\mu_k} \right) \nabla^2 c_i(\theta) \right]. \quad (11.15)$$

The Augmented Lagrangian algorithm can accept any set of three arbitrary constraint functions $c(\theta)$, $\nabla c(\theta)$, and $\nabla^2 c(\theta)$. When given the current parameter values $c(\theta)$ returns a vector of constraint values whereby each position corresponds to one of the model parameters. The constraint is defined as $c_i \geq 0$. The function $\nabla c(\theta)$ returns the matrix of

constraint gradients and $\nabla^2 c(\theta)$ is the constraint Hessian function which should return the 3D matrix of constraint Hessians.

A more specific set of constraints accepted by the Method of Multipliers are bound constraints. These are defined by the function

$$l \leq \theta \leq u, \quad (11.16)$$

where l and u are the vectors of lower and upper bounds respectively and θ is the parameter vector. For example for model-free model $m4$ to place lower and upper bounds on the order parameter and lower bounds on the correlation time and chemical exchange parameters, the vectors are

$$\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \leq \begin{pmatrix} S^2 \\ \tau_e \\ R_{ex} \end{pmatrix} \leq \begin{pmatrix} 1 \\ \infty \\ \infty \end{pmatrix}. \quad (11.17)$$

The default setting in the program relax is to use linear constraints which are defined as

$$A \cdot \theta \geq b, \quad (11.18)$$

where A is an $m \times n$ matrix where the rows are the transposed vectors a_i of length n ; the elements of a_i are the coefficients of the model parameters; θ is the vector of model parameters of dimension n ; b is the vector of scalars of dimension m ; m is the number of constraints; and n is the number of model parameters.

In rearranging (11.18) the linear constraint function $c(\theta)$ returns the vector $A \cdot \theta - b$. Because of the linearity of the constraints the gradient and Hessian are greatly simplified. The gradient $\nabla c(\theta)$ is simply the matrix A and the Hessian $\nabla^2 c(\theta)$ is zero.

11.5.2 Logarithmic barrier constraint algorithm

Another constraint method is that of the logarithmic barrier algorithm. As in the Method of Multipliers this method is iterative. The function being minimised is replaced with

$$\Phi(\theta) = \begin{cases} \epsilon \sum_{i=1}^m -\log(b_i - A_i^T \theta) & \text{if } A \cdot \theta < b, \\ +\infty & \text{otherwise.} \end{cases} \quad (11.19)$$

The value of ϵ is increased with each iteration, increase the logarithmic penalty. An advantage of this method over the Method of Multipliers is that gradients are not required.

11.6 Diagonal scaling

Model scaling can have a significant effect on the optimisation algorithm – a poorly scaled model can cause certain techniques to fail. When two parameters of the model lie on very different numeric scales the model is said to be poorly scaled. For example in model-free analysis the order of magnitude of the order parameters is one whereas for the internal

correlation times the order of magnitude is between $1e^{-12}$ to $1e^{-8}$. Most effected are the trust region algorithms – the multidimensional sphere of trust will either be completely ineffective against the correlation time parameters or severely restrict optimisation in the order parameter dimensions. Again in model-free analyses the significant scaling disparity can even cause failure of optimisation due to amplified effects of machine precision. Therefore the model parameters need to be scaled.

This can be done by supplying the optimisation algorithm with the scaled rather than unscaled parameters. When the chi-squared function, gradient, and Hessian are called the vector is then premultiplied with a diagonal matrix in which the diagonal elements are the scaling factors.

Chapter 12

Optimisation of relaxation data – values, gradients, and Hessians

12.1 Introduction to the mathematics behind the optimisation of relaxation data

A word of warning before reading this chapter, the topics covered here are quite advanced and are not necessary for understanding how to either use relax or to implement any of the data analysis techniques present within relax. The material of this chapter is intended as an in-depth explanation of the mathematics involved in the optimisation of the parameters of the model-free models, or any theory involving relaxation data. As such it contains the chi-squared equation, relaxation equations, spectral density functions, and diffusion tensor equations as well as their gradients (the vector of first partial derivatives) and Hessians (the matrix of second partial derivatives). All these equations are used in the optimisation of model-free models $m0$ to $m9$; models $tm0$ to $tm9$; the ellipsoidal, spheroidal, and spherical diffusion tensors; and the combination of the diffusion tensor and the model-free models. They also apply to all other theories involving the base R_1 , R_2 , and steady-state NOE relaxation rates.

12.2 The four parameter combinations

In model-free analysis four different combinations of parameters can be optimised, each of which requires a different approach to the construction of the chi-squared value, gradient, and Hessian. These categories depend on whether the model-free parameter set \mathfrak{F} , the diffusion tensor parameter set \mathfrak{D} , or both sets are simultaneously optimised. The addition of the local τ_m parameter to the model-free set \mathfrak{F} creates a fourth parameter combination.

12.2.1 Optimisation of the model-free models

This is the simplest category as it involves solely the optimisation of the model-free parameters of an individual residue while the diffusion tensor parameters are held constant.

The model-free parameters belong to the set \mathfrak{F}_i of the residue i . The models include $m0$ to $m9$ and the dimensionality is low with

$$\dim \mathfrak{F}_i = k \leq 5 \quad (12.1)$$

for the most complex model $m8 = \{S^2, \tau_f, S_f^2, \tau_s, R_{ex}\}$. The relaxation data of a single residue is used to build the chi-squared value, gradient, and Hessian.

12.2.2 Optimisation of the local τ_m models

The addition of the local τ_m parameter to the set \mathfrak{F}_i creates a new set of models which will be labelled \mathfrak{T}_i . These include models $tm0$ to $tm9$. The local τ_m parameter is the single member of the set \mathfrak{D}_i and in set notation

$$\mathfrak{T}_i = \mathfrak{D}_i \cup \mathfrak{F}_i. \quad (12.2)$$

Although the Brownian rotational diffusion parameter local τ_m is optimised, this category is residue specific. As such the complexity of the optimisation is lower than the next two categories. It is slightly greater than the optimisation of the set \mathfrak{F}_i as

$$\dim \mathfrak{T}_i = 1 + k \leq 6, \quad (12.3)$$

where k is the number of model-free parameters.

12.2.3 Optimisation of the diffusion tensor parameters

The parameters of the Brownian rotational diffusion tensor belong to the set \mathfrak{D} . This set is the union of the geometric parameters $\mathfrak{G} = \{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r\}$ and the orientational parameters \mathfrak{O} ,

$$\mathfrak{D} = \mathfrak{G} \cup \mathfrak{O}. \quad (12.4)$$

When diffusion is spherical solely the geometric parameter \mathfrak{D}_{iso} is optimised. When the molecule diffuses as a spheroid the geometric parameters \mathfrak{D}_{iso} and \mathfrak{D}_a and the orientational parameters θ (the polar angle) and ϕ (the azimuthal angle) are optimised. If the molecule diffuses as an ellipsoid the geometric parameters \mathfrak{D}_{iso} , \mathfrak{D}_a , and \mathfrak{D}_r are optimised together with the Euler angles α , β , and γ .

This category is defined as the optimisation of solely the parameters of \mathfrak{D} . The model-free parameters of \mathfrak{F} are held constant. As all selected residues of the macromolecule are involved in the optimisation, this category is global and can be more complex than the optimisation of \mathfrak{F}_i or \mathfrak{T}_i . The dimensionality of the problem nevertheless low with

$$\dim \mathfrak{D} = 1, \quad \dim \mathfrak{D} = 4, \quad \dim \mathfrak{D} = 6, \quad (12.5)$$

for the diffusion as a sphere, spheroid, and ellipsoid respectively.

12.2.4 Optimisation of the global model

The global model is defined as

$$\mathfrak{S} = \mathfrak{D} \cup \left(\bigcup_{i=1}^l \mathfrak{F}_i \right), \quad (12.6)$$

where i is the residue index and l is the total number of residues used in the analysis. This is the most complex of the four categories as both diffusion tensor parameters and model-free parameters of all selected residues are optimised simultaneously. The dimensionality of the model \mathfrak{S} is much greater than the other categories and is equal to

$$\dim \mathfrak{S} = \dim \mathfrak{D} + \sum_{i=1}^l k_i \leq 6 + 5l, \quad (12.7)$$

where k_i is the number of model-free parameters for the residue i and is equal to $\dim \mathfrak{F}_i$, the number six corresponds to the maximum dimensionality of \mathfrak{D} , and the number five corresponds to the maximum dimensionality of \mathfrak{F}_i .

12.3 Construction of the values, gradients, and Hessians

12.3.1 The sum of chi-squared values

For the single residue models of \mathfrak{F}_i and \mathfrak{T}_i the chi-squared value χ_i^2 which is optimised is simply Equation (12.13) on page 183 in which the relaxation data is that of residue i . However for the global models \mathfrak{D} and \mathfrak{S} in which all selected residues are involved the optimised chi-squared value is the sum of those for each residue,

$$\chi^2 = \sum_{i=1}^l \chi_i^2, \quad (12.8)$$

where i is the residue index and l is the total number of residues used in the analysis. This is equivalent to Equation (12.13) when the index i ranges over the relaxation data of all selected residues.

12.3.2 Construction of the gradient

The construction of the gradient is significantly different for the models \mathfrak{F}_i , \mathfrak{T}_i , \mathfrak{D} , and \mathfrak{S} . In Figure 12.1 the construction of the chi-squared gradient $\nabla \chi^2$ for the global model \mathfrak{S} is demonstrated. In this case

$$\nabla \chi^2 = \sum_{i=1}^l \nabla \chi_i^2, \quad (12.9)$$

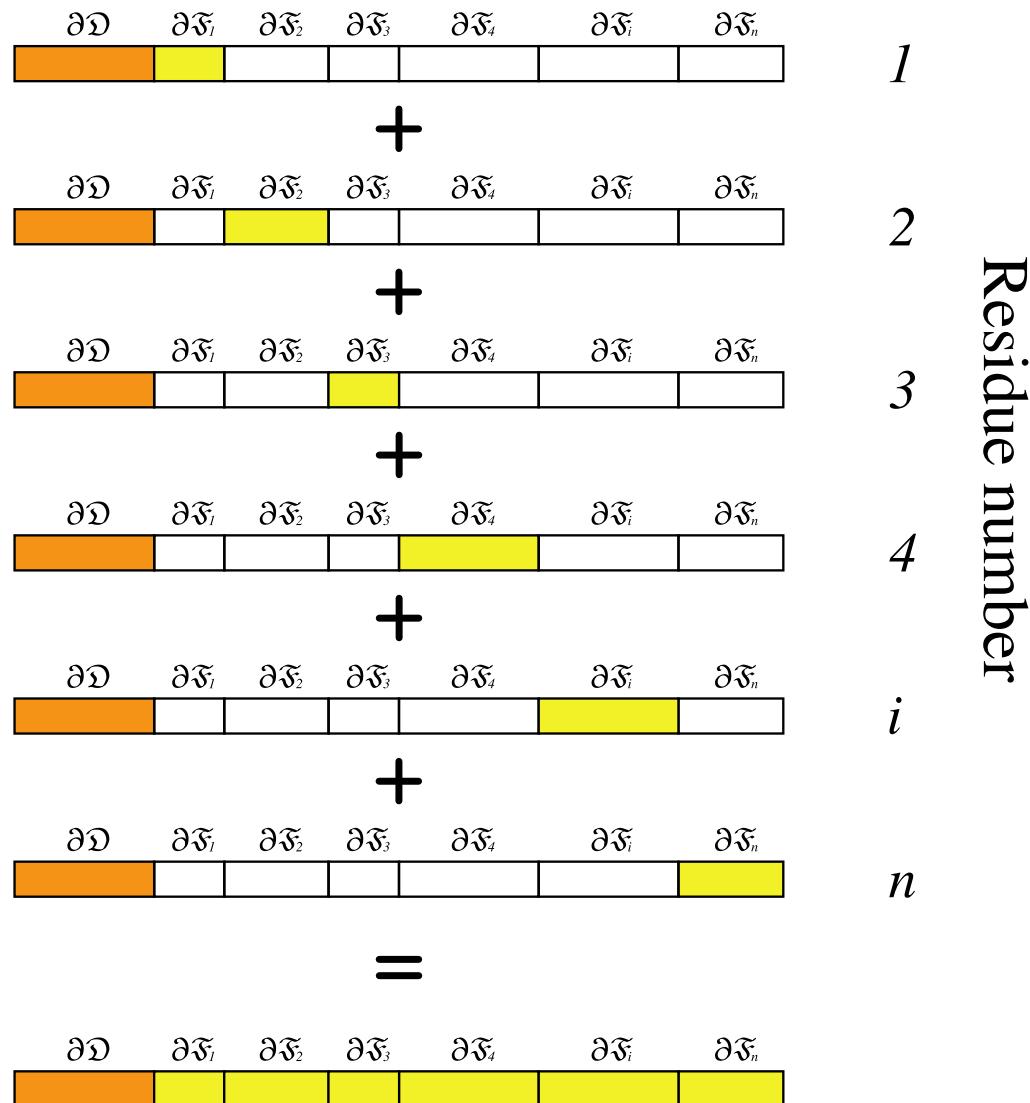


Figure 12.1: The construction of the model-free gradient $\nabla\chi^2$ for the global model \mathfrak{S} . For each residue i a different vector $\nabla\chi^2_i$ is constructed. The first element of the vector represented by the symbol $\partial\mathfrak{D}$ (the orange block) is the sub-vector of chi-squared partial derivatives with respect to each of the diffusion tensor parameters \mathfrak{D}_j . The rest of the elements, grouped into blocks for each residue denoted by the symbol $\partial\mathfrak{F}_i$, are the sub-vectors of chi-squared partial derivatives with respect to each of the model-free parameters \mathfrak{F}_i^j . For the residue dependent vector $\nabla\chi^2_i$ the partial derivatives with respect to the model-free parameters of \mathfrak{F}_j where $i \neq j$ are zero. These blocks are left uncoloured. The complete gradient of \mathfrak{S} is the sum of the vectors $\nabla\chi^2_i$.

where $\nabla\chi_i^2$ is the vector of partial derivatives of the chi-squared equation χ_i^2 for the residue i . The length of this vector is

$$\|\nabla\chi_i^2\| = \dim \mathfrak{S}, \quad (12.10)$$

with each position of the vector j equal to $\frac{\partial\chi_i^2}{\partial\theta_j}$ where each θ_j is a parameter of the model.

The construction of the gradient $\nabla\chi^2$ for the model \mathfrak{D} is simply a subset of that of \mathfrak{S} . This is demonstrated in Figure 12.1 by simply taking the component of the gradient $\nabla\chi_i^2$ denoted by the symbol $\partial\mathfrak{D}$ (the orange blocks) and summing these for all residues. This sum is given by (12.9) and

$$\|\nabla\chi^2\| = \dim \mathfrak{D}. \quad (12.11)$$

For the parameter set \mathfrak{T}_i , which consists of the local τ_m parameter and the model-free parameters of a single residue, the gradient $\nabla\chi_i^2$ for the residue i is simply the combination of the single orange block and single yellow block of the index i (Figure 12.1).

The model-free parameter set \mathfrak{F}_i is even simpler. In Figure 12.1 the gradient $\nabla\chi_i^2$ is simply the vector denoted by the single yellow block for the residue i .

12.3.3 Construction of the Hessian

The construction of the Hessian for the models \mathfrak{F}_i , \mathfrak{T}_i , \mathfrak{D} , and \mathfrak{S} is very similar to the procedure used for the gradient. The chi-squared Hessian for the global models \mathfrak{D} and \mathfrak{S} is

$$\nabla^2\chi^2 = \sum_{i=1}^l \nabla^2\chi_i^2. \quad (12.12)$$

Figure 12.2 demonstrates the construction of the full Hessian for the model \mathfrak{S} . The Hessian for the model \mathfrak{D} is the sum of all the red blocks. The Hessian for the model \mathfrak{T}_i is the combination of the single red block for residue i , the two orange blocks representing the sub-matrices of chi-squared second partial derivatives with respect to the diffusion parameter \mathfrak{D}_j and the model-free parameter \mathfrak{F}_i^k , and the single yellow block for that residue. The Hessian for the model-free model \mathfrak{F}_i is simply the sub-matrix for the residue i coloured yellow.

12.4 The value, gradient, and Hessian dependency chain

The dependency chain which was outlined in the model-free chapter – that the chi-squared function is dependent on the transformed relaxation equations which are dependent on the relaxation equations which themselves are dependent on the spectral density functions – combine with the values, gradients, and Hessians to create a complex web of dependencies. The relationship between all the values, gradients, and Hessians are outlined in Figure 12.3.

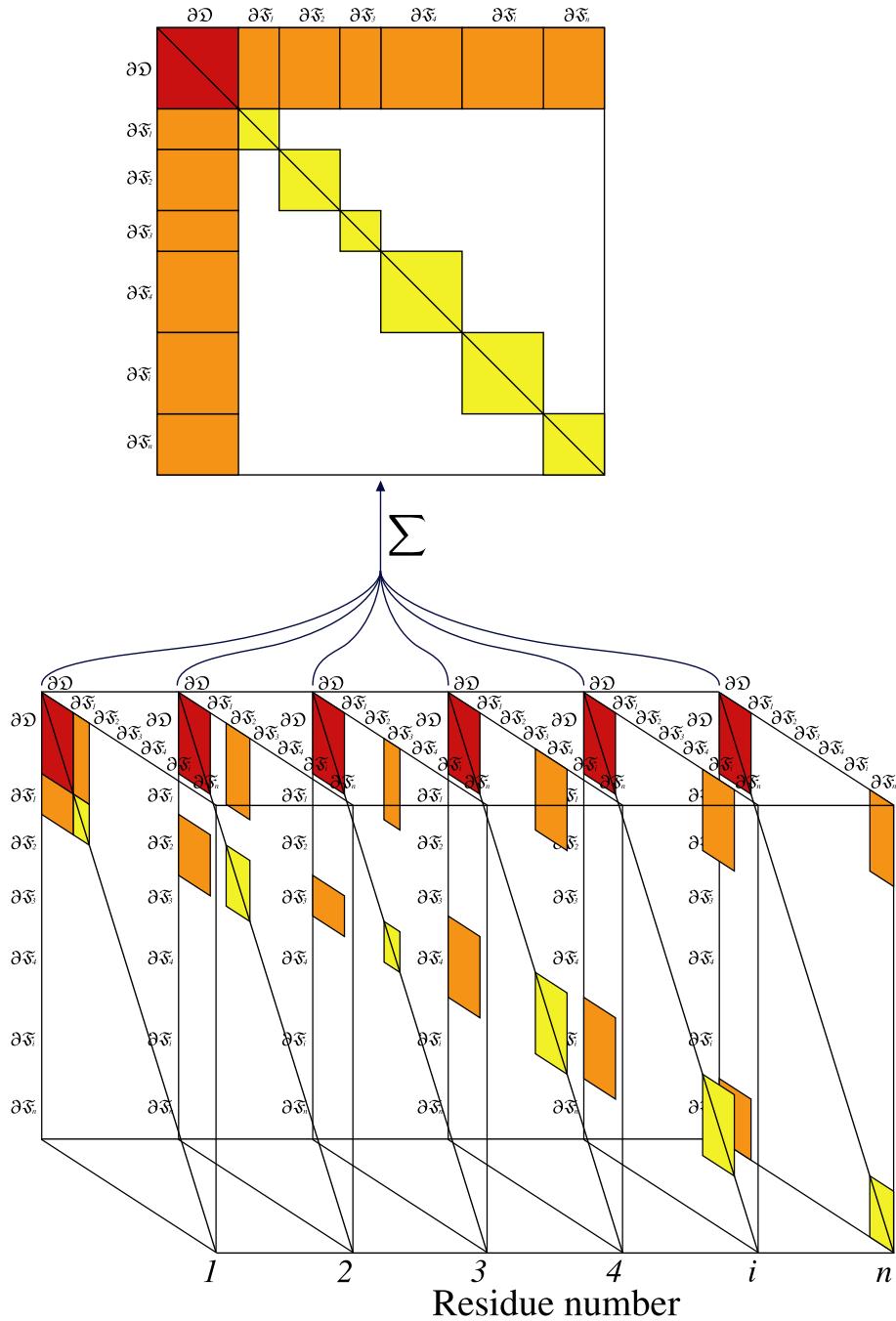


Figure 12.2: The model-free Hessian kite – a demonstration of the construction of the model-free Hessian $\nabla^2\chi^2$ for the global model \mathfrak{G} . For each residue i a different matrix $\nabla^2\chi_i^2$ is constructed. The first element of the matrix represented by the two symbols $\partial\mathfrak{D}$ (the red block) is the sub-matrix of chi-squared second partial derivatives with respect to the diffusion tensor parameters \mathfrak{D}_j and \mathfrak{D}_k . The orange blocks are the sub-matrices of chi-squared second partial derivatives with respect to the diffusion parameter \mathfrak{D}_j and the model-free parameter \mathfrak{F}_i^k . The yellow blocks are the sub-matrices of chi-squared second partial derivatives with respect to the model-free parameters \mathfrak{F}_i^j and \mathfrak{F}_i^k . For the residue dependent matrix $\nabla^2\chi_i^2$ the second partial derivatives with respect to the model-free parameters \mathfrak{F}_l^j and \mathfrak{F}_l^k where $i \neq l$ are zero. In addition, the second partial derivatives with respect to the model-free parameters \mathfrak{F}_i^j and \mathfrak{F}_i^k where $i \neq l$ are also zero. These blocks of sub-matrices are left uncoloured. The complete Hessian of \mathfrak{G} is the sum of the matrices $\nabla^2\chi_i^2$.

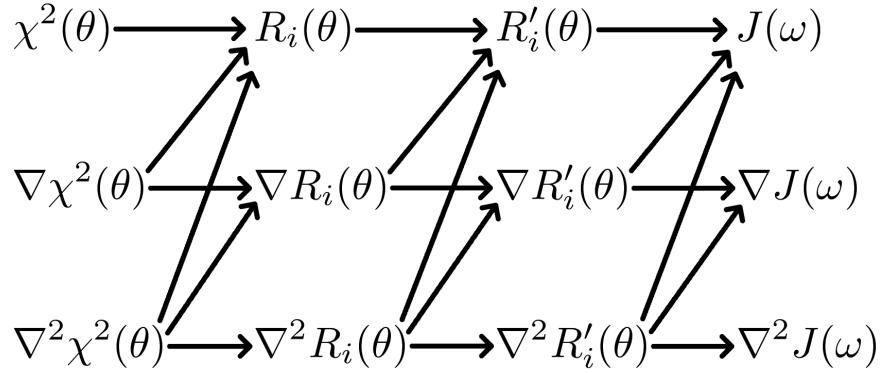


Figure 12.3: Dependencies between the χ^2 , transformed relaxation, relaxation, and spectral density equations, gradients, and Hessians.

12.5 The χ^2 value, gradient, and Hessian

12.5.1 The χ^2 value

The χ^2 value is defined as

$$\chi^2(\theta) = \sum_{i=1}^n \frac{(R_i - R_i(\theta))^2}{\sigma_i^2}, \quad (12.13)$$

where the summation index i ranges over all the relaxation data of all residues used in the analysis.

12.5.2 The χ^2 gradient

The χ^2 gradient in vector notation is

$$\nabla \chi^2(\theta) = 2 \sum_{i=1}^n \frac{(R_i - R_i(\theta))^2}{\sigma_i^2} \nabla R_i(\theta). \quad (12.14)$$

12.5.3 The χ^2 Hessian

The χ^2 Hessian in vector notation is

$$\nabla^2 \chi^2(\theta) = 2 \sum_{i=1}^n \frac{1}{\sigma_i^2} (\nabla R_i(\theta) \cdot \nabla R_i(\theta)^T - (R_i - R_i(\theta)) \nabla^2 R_i(\theta)). \quad (12.15)$$

12.6 The $R_i(\theta)$ values, gradients, and Hessians

12.6.1 The $R_i(\theta)$ values

The $R_i(\theta)$ values are given by

$$R_1(\theta) = R'_1(\theta), \quad (12.16a)$$

$$R_2(\theta) = R'_2(\theta), \quad (12.16b)$$

$$\text{NOE}(\theta) = 1 + \frac{\gamma_H}{\gamma_X} \frac{\sigma_{\text{NOE}}(\theta)}{R_1(\theta)}. \quad (12.16c)$$

12.6.2 The $R_i(\theta)$ gradients

The $R_i(\theta)$ gradients in vector notation are

$$\nabla R_1(\theta) = \nabla R'_1(\theta), \quad (12.17a)$$

$$\nabla R_2(\theta) = \nabla R'_2(\theta), \quad (12.17b)$$

$$\nabla \text{NOE}(\theta) = \frac{\gamma_H}{\gamma_X} \frac{1}{R_1(\theta)^2} \left(R_1(\theta) \nabla \sigma_{\text{NOE}}(\theta) - \sigma_{\text{NOE}}(\theta) \nabla R_1(\theta) \right). \quad (12.17c)$$

12.6.3 The $R_i(\theta)$ Hessians

The $R_i(\theta)$ Hessians in vector notation are

$$\nabla^2 R_1(\theta) = \nabla^2 R'_1(\theta), \quad (12.18a)$$

$$\nabla^2 R_2(\theta) = \nabla^2 R'_2(\theta), \quad (12.18b)$$

$$\begin{aligned} \nabla^2 \text{NOE}(\theta) = & \frac{\gamma_H}{\gamma_X} \frac{1}{R_1(\theta)^3} \left[\sigma_{\text{NOE}}(\theta) \left(2 \nabla R_1(\theta) \cdot \nabla R_1(\theta)^T - R_1(\theta) \nabla^2 R_1(\theta) \right) \right. \\ & \left. - R_1(\theta) \left(\nabla \sigma_{\text{NOE}}(\theta) \cdot \nabla R_1(\theta)^T - R_1(\theta) \nabla^2 \sigma_{\text{NOE}}(\theta) \right) \right]. \end{aligned} \quad (12.18c)$$

12.7 $R'_i(\theta)$ values, gradients, and Hessians

The partial and second partial derivatives of the relaxation equations of the set $R'(\theta)$ are different for each parameter of the vector θ . The vector representation of the gradient $\nabla R'_i(\theta)$ and the matrix representation of the Hessian $\nabla^2 R'_i(\theta)$ can be reconstructed from the individual elements presented in the next section.

12.7.1 Components of the $R'_i(\theta)$ equations

To simplify the calculations of the gradients and Hessians the $R'_i(\theta)$ equations have been broken down into a number of components. These include the dipolar and CSA constants as well as the dipolar and CSA spectral density terms for each of the three transformed relaxation data types $\{R_1, R_2, \sigma_{\text{NOE}}\}$. The segregation of these components simplifies the maths as many partial derivatives of the components are zero.

Dipolar constant

The dipolar constant is defined as

$$d = \frac{1}{4} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{(\gamma_H \gamma_X \hbar)^2}{\langle r^6 \rangle}. \quad (12.19)$$

This component of the relaxation equations is independent of the parameter of the spectral density function θ_j , the chemical exchange parameter ρ_{ex} , and the CSA parameter $\Delta\sigma$. Therefore the partial and second partial derivatives with respect to these parameters is zero. Only the derivative with respect to the bond length r is non-zero being

$$d' \equiv \frac{dd}{dr} = -\frac{3}{2} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{(\gamma_H \gamma_X \hbar)^2}{\langle r^7 \rangle}. \quad (12.20)$$

The second derivative with respect to the bond length is

$$d'' \equiv \frac{d^2d}{dr^2} = \frac{21}{2} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{(\gamma_H \gamma_X \hbar)^2}{\langle r^8 \rangle}. \quad (12.21)$$

CSA constant

The CSA constant is defined as

$$c = \frac{(\omega_X \cdot \Delta\sigma)^2}{3}. \quad (12.22)$$

The partial derivative of this component with respect to all parameters but the CSA parameter $\Delta\sigma$ is zero. This derivative is

$$c' \equiv \frac{dc}{d\Delta\sigma} = \frac{2\omega_X^2 \cdot \Delta\sigma}{3}. \quad (12.23)$$

The CSA constant second derivative with respect to $\Delta\sigma$ is

$$c'' \equiv \frac{d^2c}{d\Delta\sigma^2} = \frac{2\omega_X^2}{3}. \quad (12.24)$$

R_{ex} constant

The R_{ex} constant is defined as

$$R_{ex} = \rho_{ex}(2\pi\omega_H)^2. \quad (12.25)$$

The partial derivative of this component with respect to all parameters but the chemical exchange parameter ρ_{ex} is zero. This derivative is

$$R'_{ex} \equiv \frac{dR_{ex}}{d\rho_{ex}} = (2\pi\omega_H)^2. \quad (12.26)$$

The R_{ex} constant second derivative with respect to ρ_{ex} is

$$R''_{ex} \equiv \frac{d^2R_{ex}}{d\rho_{ex}^2} = 0. \quad (12.27)$$

Spectral density terms of the R_1 dipolar component

For the dipolar component of the R_1 equation (7.2a) on page 84 the spectral density terms are

$$J_d^{R_1} = J(\omega_H - \omega_X) + 3J(\omega_X) + 6J(\omega_H + \omega_X). \quad (12.28)$$

The partial derivative of these terms with respect to the spectral density function parameter θ_j is

$$J_d^{R_1'} \equiv \frac{\partial J_d^{R_1}}{\partial \theta_j} = \frac{\partial J(\omega_H - \omega_X)}{\partial \theta_j} + 3 \frac{\partial J(\omega_X)}{\partial \theta_j} + 6 \frac{\partial J(\omega_H + \omega_X)}{\partial \theta_j}. \quad (12.29)$$

The second partial derivative with respect to the spectral density function parameters θ_j and θ_k is

$$J_d^{R_1''} \equiv \frac{\partial^2 J_d^{R_1}}{\partial \theta_j \cdot \partial \theta_k} = \frac{\partial^2 J(\omega_H - \omega_X)}{\partial \theta_j \cdot \partial \theta_k} + 3 \frac{\partial^2 J(\omega_X)}{\partial \theta_j \cdot \partial \theta_k} + 6 \frac{\partial^2 J(\omega_H + \omega_X)}{\partial \theta_j \cdot \partial \theta_k}. \quad (12.30)$$

Spectral density terms of the R_1 CSA component

For the CSA component of the R_1 equation (7.2a) on page 84 the spectral density terms are

$$J_c^{R_1} = J(\omega_X). \quad (12.31)$$

The partial derivative of these terms with respect to the spectral density function parameter θ_j is

$$J_c^{R_1'} \equiv \frac{\partial J_c^{R_1}}{\partial \theta_j} = \frac{\partial J(\omega_X)}{\partial \theta_j}. \quad (12.32)$$

The second partial derivative with respect to the spectral density function parameters θ_j and θ_k is

$$J_c^{R_1''} \equiv \frac{\partial^2 J_c^{R_1}}{\partial \theta_j \cdot \partial \theta_k} = \frac{\partial^2 J(\omega_X)}{\partial \theta_j \cdot \partial \theta_k}. \quad (12.33)$$

Spectral density terms of the R_2 dipolar component

For the dipolar component of the R_2 equation (7.2b) on page 84 the spectral density terms are

$$J_d^{R_2} = 4J(0) + J(\omega_H - \omega_X) + 3J(\omega_X) + 6J(\omega_H) + 6J(\omega_H + \omega_X). \quad (12.34)$$

The partial derivative of these terms with respect to the spectral density function parameter θ_j is

$$J_d^{R_2'} \equiv \frac{\partial J_d^{R_2}}{\partial \theta_j} = 4 \frac{\partial J(0)}{\partial \theta_j} + \frac{\partial J(\omega_H - \omega_X)}{\partial \theta_j} + 3 \frac{\partial J(\omega_X)}{\partial \theta_j} + 6 \frac{\partial J(\omega_H)}{\partial \theta_j} + 6 \frac{\partial J(\omega_H + \omega_X)}{\partial \theta_j}. \quad (12.35)$$

The second partial derivative with respect to the spectral density function parameters θ_j and θ_k is

$$\begin{aligned} J_d^{R_2''} \equiv \frac{\partial^2 J_d^{R_2}}{\partial \theta_j \cdot \partial \theta_k} &= 4 \frac{\partial^2 J(0)}{\partial \theta_j \cdot \partial \theta_k} + \frac{\partial^2 J(\omega_H - \omega_X)}{\partial \theta_j \cdot \partial \theta_k} + 3 \frac{\partial^2 J(\omega_X)}{\partial \theta_j \cdot \partial \theta_k} \\ &\quad + 6 \frac{\partial^2 J(\omega_H)}{\partial \theta_j \cdot \partial \theta_k} + 6 \frac{\partial^2 J(\omega_H + \omega_X)}{\partial \theta_j \cdot \partial \theta_k}. \end{aligned} \quad (12.36)$$

Spectral density terms of the R_2 CSA component

For the CSA component of the R_2 equation (7.2b) on page 84 the spectral density terms are

$$J_c^{R_2} = 4J(0) + 3J(\omega_X). \quad (12.37)$$

The partial derivative of these terms with respect to the spectral density function parameter θ_j is

$$J_c^{R_2'} \equiv \frac{\partial J_c^{R_2}}{\partial \theta_j} = 4 \frac{\partial J(0)}{\partial \theta_j} + 3 \frac{\partial J(\omega_X)}{\partial \theta_j}. \quad (12.38)$$

The second partial derivative with respect to the spectral density function parameters θ_j and θ_k is

$$J_c^{R_2''} \equiv \frac{\partial^2 J_c^{R_2}}{\partial \theta_j \cdot \partial \theta_k} = 4 \frac{\partial^2 J(0)}{\partial \theta_j \cdot \partial \theta_k} + 3 \frac{\partial^2 J(\omega_X)}{\partial \theta_j \cdot \partial \theta_k}. \quad (12.39)$$

Spectral density terms of the σ_{NOE} dipolar component

For the dipolar component of the σ_{NOE} equation (7.2c) on page 84 the spectral density terms are

$$J_d^{\sigma_{\text{NOE}}} = 6J(\omega_H + \omega_X) - J(\omega_H - \omega_X). \quad (12.40)$$

The partial derivative of these terms with respect to the spectral density function parameter θ_j is

$$J_d^{\sigma_{\text{NOE}}'} \equiv \frac{\partial J_d^{\sigma_{\text{NOE}}}}{\partial \theta_j} = 6 \frac{\partial J(\omega_H + \omega_X)}{\partial \theta_j} - \frac{\partial J(\omega_H - \omega_X)}{\partial \theta_j}. \quad (12.41)$$

The second partial derivative with respect to the spectral density function parameters θ_j and θ_k is

$$J_d^{\sigma_{\text{NOE}}''} \equiv \frac{\partial^2 J_d^{\sigma_{\text{NOE}}}}{\partial \theta_j \cdot \partial \theta_k} = 6 \frac{\partial^2 J(\omega_H + \omega_X)}{\partial \theta_j \cdot \partial \theta_k} - \frac{\partial^2 J(\omega_H - \omega_X)}{\partial \theta_j \cdot \partial \theta_k}. \quad (12.42)$$

12.7.2 $R'_i(\theta)$ values

Using the components of the relaxation equations defined above the three relaxation equations can be re-expressed as

$$R_1(\theta) = dJ_d^{R_1} + cJ_c^{R_1}, \quad (12.43a)$$

$$R_2(\theta) = \frac{d}{2}J_d^{R_2} + \frac{c}{6}J_c^{R_2}, \quad (12.43b)$$

$$\sigma_{\text{NOE}}(\theta) = dJ_d^{\sigma_{\text{NOE}}}. \quad (12.43c)$$

12.7.3 $R'_i(\theta)$ gradients

A different partial derivative exists for the spectral density function parameter θ_j , the chemical exchange parameter ρ_{ex} , CSA parameter $\Delta\sigma$, and bond length parameter r . In model-free analysis the spectral density parameters include both the parameters of the diffusion tensor and the parameters of the various model-free models.

θ_j partial derivative

The partial derivatives of the relaxation equations with respect to the spectral density function parameter θ_j are

$$\frac{\partial R_1(\theta)}{\partial \theta_j} = dJ_d^{R_1'} + cJ_c^{R_1'}, \quad (12.44a)$$

$$\frac{\partial R_2(\theta)}{\partial \theta_j} = \frac{d}{2}J_d^{R_2'} + \frac{c}{6}J_c^{R_2'}, \quad (12.44b)$$

$$\frac{\partial \sigma_{\text{NOE}}(\theta)}{\partial \theta_j} = dJ_d^{\sigma_{\text{NOE}}'}. \quad (12.44c)$$

ρ_{ex} partial derivative

The partial derivatives of the relaxation equations with respect to the chemical exchange parameter ρ_{ex} are

$$\frac{\partial R_1(\theta)}{\partial \rho_{ex}} = 0, \quad (12.45a)$$

$$\frac{\partial R_2(\theta)}{\partial \rho_{ex}} = (2\pi\omega_H)^2, \quad (12.45b)$$

$$\frac{\partial \sigma_{\text{NOE}}(\theta)}{\partial \rho_{ex}} = 0. \quad (12.45c)$$

$\Delta\sigma$ partial derivative

The partial derivatives of the relaxation equations with respect to the CSA parameter $\Delta\sigma$ are

$$\frac{\partial R_1(\theta)}{\partial \Delta\sigma} = c' J_c^{R_1}, \quad (12.46a)$$

$$\frac{\partial R_2(\theta)}{\partial \Delta\sigma} = \frac{c'}{6} J_c^{R_2}, \quad (12.46b)$$

$$\frac{\partial \sigma_{NOE}(\theta)}{\partial \Delta\sigma} = 0. \quad (12.46c)$$

 r partial derivative

The partial derivatives of the relaxation equations with respect to the bond length parameter r are

$$\frac{\partial R_1(\theta)}{\partial r} = d' J_d^{R_1}, \quad (12.47a)$$

$$\frac{\partial R_2(\theta)}{\partial r} = \frac{d'}{2} J_d^{R_2}, \quad (12.47b)$$

$$\frac{\partial \sigma_{NOE}(\theta)}{\partial r} = d' J_d^{\sigma_{NOE}}. \quad (12.47c)$$

12.7.4 $R'_i(\theta)$ Hessians

Again different second partial derivatives with respect to the spectral density function parameters θ_j and θ_k , the chemical exchange parameter ρ_{ex} , CSA parameter $\Delta\sigma$, and bond length parameter r . These second partial derivatives are the components of the $R'_i(\theta)$ Hessian matrices.

 $\theta_j - \theta_k$ partial derivative

The second partial derivatives of the relaxation equations with respect to the spectral density function parameters θ_j and θ_k are

$$\frac{\partial^2 R_1(\theta)}{\partial \theta_j \cdot \partial \theta_k} = d J_d^{R_1''} + c J_c^{R_1''}, \quad (12.48a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \theta_j \cdot \partial \theta_k} = \frac{d}{2} J_d^{R_2''} + \frac{c}{6} J_c^{R_2''}, \quad (12.48b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \theta_j \cdot \partial \theta_k} = d J_d^{\sigma_{NOE}''}. \quad (12.48c)$$

$\theta_j - \rho_{ex}$ partial derivative

The second partial derivatives of the relaxation equations with respect to the spectral density function parameter θ_j and the chemical exchange parameter ρ_{ex} are

$$\frac{\partial^2 R_1(\theta)}{\partial \theta_j \cdot \partial \rho_{ex}} = 0, \quad (12.49a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \theta_j \cdot \partial \rho_{ex}} = 0, \quad (12.49b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \theta_j \cdot \partial \rho_{ex}} = 0. \quad (12.49c)$$

 $\theta_j - \Delta\sigma$ partial derivative

The second partial derivatives of the relaxation equations with respect to the spectral density function parameter θ_j and the CSA parameter $\Delta\sigma$ are

$$\frac{\partial^2 R_1(\theta)}{\partial \theta_j \cdot \partial \Delta\sigma} = c' J_c^{R_1'}, \quad (12.50a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \theta_j \cdot \partial \Delta\sigma} = \frac{c'}{6} J_c^{R_2'}, \quad (12.50b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \theta_j \cdot \partial \Delta\sigma} = 0. \quad (12.50c)$$

 $\theta_j - r$ partial derivative

The second partial derivatives of the relaxation equations with respect to the spectral density function parameter θ_j and the bond length parameter r are

$$\frac{\partial^2 R_1(\theta)}{\partial \theta_j \cdot \partial r} = d' J_d^{R_1'}, \quad (12.51a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \theta_j \cdot \partial r} = \frac{d'}{2} J_d^{R_2'}, \quad (12.51b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \theta_j \cdot \partial r} = d' J_d^{\sigma_{NOE}'}. \quad (12.51c)$$

 $\rho_{ex} - \rho_{ex}$ partial derivative

The second partial derivatives of the relaxation equations with respect to the chemical exchange parameter ρ_{ex} twice are

$$\frac{\partial^2 R_1(\theta)}{\partial \rho_{ex}^2} = 0, \quad (12.52a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \rho_{ex}^2} = 0, \quad (12.52b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \rho_{ex}^2} = 0. \quad (12.52c)$$

$\rho_{ex} - \Delta\sigma$ partial derivative

The second partial derivatives of the relaxation equations with respect to the chemical exchange parameter ρ_{ex} and the CSA parameter $\Delta\sigma$ are

$$\frac{\partial^2 R_1(\theta)}{\partial \rho_{ex} \cdot \partial \Delta\sigma} = 0, \quad (12.53a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \rho_{ex} \cdot \partial \Delta\sigma} = 0, \quad (12.53b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \rho_{ex} \cdot \partial \Delta\sigma} = 0. \quad (12.53c)$$

 $\rho_{ex} - r$ partial derivative

The second partial derivatives of the relaxation equations with respect to the chemical exchange parameter ρ_{ex} and the bond length parameter r are

$$\frac{\partial^2 R_1(\theta)}{\partial \rho_{ex} \cdot \partial r} = 0, \quad (12.54a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \rho_{ex} \cdot \partial r} = 0, \quad (12.54b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \rho_{ex} \cdot \partial r} = 0. \quad (12.54c)$$

 $\Delta\sigma - \Delta\sigma$ partial derivative

The second partial derivatives of the relaxation equations with respect to the CSA parameter $\Delta\sigma$ twice are

$$\frac{\partial^2 R_1(\theta)}{\partial \Delta\sigma^2} = c'' J_c^{R_1}, \quad (12.55a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \Delta\sigma^2} = \frac{c''}{6} J_c^{R_2}, \quad (12.55b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \Delta\sigma^2} = 0. \quad (12.55c)$$

 $\Delta\sigma - r$ partial derivative

The second partial derivatives of the relaxation equations with respect to the CSA parameter $\Delta\sigma$ and the bond length parameter r are

$$\frac{\partial^2 R_1(\theta)}{\partial \Delta\sigma \cdot \partial r} = 0, \quad (12.56a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial \Delta\sigma \cdot \partial r} = 0, \quad (12.56b)$$

$$\frac{\partial^2 \sigma_{NOE}(\theta)}{\partial \Delta\sigma \cdot \partial r} = 0. \quad (12.56c)$$

$r - r$ partial derivative

The second partial derivatives of the relaxation equations with respect to the bond length parameter r twice are

$$\frac{\partial^2 R_1(\theta)}{\partial r^2} = d'' J_d^{R_1}, \quad (12.57a)$$

$$\frac{\partial^2 R_2(\theta)}{\partial r^2} = \frac{d''}{2} J_d^{R_2}, \quad (12.57b)$$

$$\frac{\partial^2 \sigma_{\text{NOE}}(\theta)}{\partial r^2} = d'' J_d^{\sigma_{\text{NOE}}}. \quad (12.57c)$$

12.8 Model-free analysis

12.8.1 The model-free equations

In the original model-free analysis of [Lipari and Szabo \(1982a\)](#) the correlation function $C(\tau)$ of the XH bond vector is approximated by decoupling the internal fluctuations of the bond vector $C_I(\tau)$ from the correlation function of the overall Brownian rotational diffusion $C_O(\tau)$ by the equation

$$C(\tau) = C_O(\tau) \cdot C_I(\tau). \quad (12.58)$$

The overall correlation functions of the diffusion of a sphere, spheroid, and ellipsoid are presented respectively in section [12.9.1](#) on page [205](#), section [12.10.1](#) on page [218](#), and section [12.11.1](#) on page [222](#). These three different equations can be combined into one generic correlation function which is independent of the type of diffusion. This generic correlation function is

$$C_O(\tau) = \frac{1}{5} \sum_{i=-k}^k c_i \cdot e^{-\tau/\tau_i}, \quad (12.59)$$

where c_i are the weights and τ_i are correlation times of the exponential terms. In the original model-free analysis of [Lipari and Szabo \(1982a,b\)](#) the internal motions are modelled by the correlation function

$$C_I(\tau) = S^2 + (1 - S^2)e^{-\tau/\tau_e}, \quad (12.60)$$

where S^2 is the generalised Lipari and Szabo order parameter which is related to the amplitude of the motion and τ_e is the effective correlation time which is an indicator of the timescale of the motion, albeit being dependent on the value of the order parameter. The order parameter ranges from one for complete rigidity to zero for unrestricted motions. Model-free theory was extended by [Clore et al. \(1990\)](#) to include motions on two timescales by the correlation function

$$C_I(\tau) = S^2 + (1 - S_f^2)e^{-\tau/\tau_f} + (S_f^2 - S^2)e^{-\tau/\tau_s}, \quad (12.61)$$

where the faster of the motions is defined by the order parameter S_f^2 and the correlation time τ_f , the slower by the parameters S_s^2 and τ_s , and the two order parameter are related by the equation $S^2 = S_f^2 \cdot S_s^2$.

The relaxation equations of [Abragam \(1961\)](#) are composed of a sum of power spectral density functions $J(\omega)$ at five frequencies. The spectral density function is related to the correlation function as the two are a Fourier pair. Applying the Fourier transform to the correlation function composed of the generic diffusion equation and the original model-free correlation function results in the equation

$$J(\omega) = \frac{2}{5} \sum_{i=-k}^k c_i \cdot \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right). \quad (12.62)$$

The Fourier transform using the extended model-free correlation function is

$$J(\omega) = \frac{2}{5} \sum_{i=-k}^k c_i \cdot \tau_i \left(\frac{S^2}{1 + (\omega\tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega\tau_f\tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega\tau_s\tau_i)^2} \right). \quad (12.63)$$

12.8.2 The original model-free gradient

The model-free gradient of the original spectral density function (12.62) is the vector of partial derivatives of the function with respect to the geometric parameter \mathfrak{G}_i , the orientational parameter \mathfrak{O}_i , the order parameter S^2 , and the internal correlation time τ_e . The positions in the vector correspond to the model parameters which are being optimised.

\mathfrak{G}_j partial derivative

The partial derivative of (12.62) with respect to the geometric parameter \mathfrak{G}_j is

$$\begin{aligned} \frac{\partial J(\omega)}{\partial \mathfrak{G}_j} = & \frac{2}{5} \sum_{i=-k}^k \left(c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \left(S^2 \frac{1 - (\omega\tau_i)^2}{(1 + (\omega\tau_i)^2)^2} + (1 - S^2) \tau_e^2 \frac{(\tau_e + \tau_i)^2 - (\omega\tau_e\tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega\tau_e\tau_i)^2)^2} \right) \right. \\ & \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i \left(\frac{S^2}{1 + (\omega\tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega\tau_e\tau_i)^2} \right) \right). \end{aligned} \quad (12.64)$$

\mathfrak{O}_j partial derivative

The partial derivative of (12.62) with respect to the orientational parameter \mathfrak{O}_j is

$$\frac{\partial J(\omega)}{\partial \mathfrak{O}_j} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i \left(\frac{S^2}{1 + (\omega\tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega\tau_e\tau_i)^2} \right). \quad (12.65)$$

S^2 partial derivative

The partial derivative of (12.62) with respect to the order parameter S^2 is

$$\frac{\partial J(\omega)}{\partial S^2} = \frac{2}{5} \sum_{i=-k}^k c_i \tau_i \left(\frac{1}{1 + (\omega\tau_i)^2} - \frac{(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega\tau_e\tau_i)^2} \right). \quad (12.66)$$

τ_e partial derivative

The partial derivative of (12.62) with respect to the correlation time τ_e is

$$\frac{\partial J(\omega)}{\partial \tau_e} = \frac{2}{5} (1 - S^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_e + \tau_i)^2 - (\omega\tau_e\tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega\tau_e\tau_i)^2)^2}. \quad (12.67)$$

12.8.3 The original model-free Hessian

The model-free Hessian of the original spectral density function (12.62) is the matrix of second partial derivatives. The matrix coordinates correspond to the model parameters which are being optimised.

$\mathfrak{G}_j - \mathfrak{G}_k$ partial derivative

The second partial derivative of (12.62) with respect to the geometric parameters \mathfrak{G}_j and \mathfrak{G}_k is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} = & \frac{2}{5} \sum_{i=-k}^k \left(-2c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \cdot \frac{\partial \tau_i}{\partial \mathfrak{G}_k} \left(S^2 \omega^2 \tau_i \frac{3 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^3} \right. \right. \\ & \left. \left. + (1 - S^2) \tau_e^2 \frac{(\tau_e + \tau_i)^3 + 3\omega^2 \tau_e^3 \tau_i (\tau_e + \tau_i) - (\omega \tau_e)^4 \tau_i^3}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^3} \right) \right. \\ & \left. + \left(\frac{\partial \tau_i}{\partial \mathfrak{G}_j} \cdot \frac{\partial c_i}{\partial \mathfrak{G}_k} + \frac{\partial \tau_i}{\partial \mathfrak{G}_k} \cdot \frac{\partial c_i}{\partial \mathfrak{G}_j} + c_i \frac{\partial^2 \tau_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} \right) \left(S^2 \frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} \right. \right. \\ & \left. \left. + (1 - S^2) \tau_e^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2} \right) \right. \\ & \left. + \left(\frac{\partial^2 c_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right) \right) \right). \quad (12.68) \end{aligned}$$

$\mathfrak{G}_j - \mathfrak{O}_k$ partial derivative

The second partial derivative of (12.62) with respect to the geometric parameter \mathfrak{G}_j and the orientational parameter \mathfrak{O}_k is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{O}_k} = & \frac{2}{5} \sum_{i=-k}^k \left(\frac{\partial \tau_i}{\partial \mathfrak{G}_j} \frac{\partial c_i}{\partial \mathfrak{O}_k} \left(S^2 \frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} + (1 - S^2) \tau_e^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2} \right) \right. \\ & \left. + \frac{\partial^2 c_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{O}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right) \right). \quad (12.69) \end{aligned}$$

$\mathfrak{G}_j - S^2$ partial derivative

The second partial derivative of (12.62) with respect to the geometric parameter \mathfrak{G}_j and the order parameter S^2 is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial S^2} = & \frac{2}{5} \sum_{i=-k}^k \left(c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \left(\frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} - \tau_e^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2} \right) \right. \\ & \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i \left(\frac{1}{1 + (\omega \tau_i)^2} - \frac{(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right) \right). \quad (12.70) \end{aligned}$$

$\mathfrak{G}_j - \tau_e$ partial derivative

The second partial derivative of (12.62) with respect to the geometric parameter \mathfrak{G}_j and the correlation time τ_e is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \tau_e} = & \frac{2}{5}(1-S^2) \sum_{i=-k}^k \left(2c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \tau_e \tau_i (\tau_e + \tau_i) \frac{(\tau_e + \tau_i)^2 - 3(\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^3} \right. \\ & \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2} \right). \quad (12.71) \end{aligned}$$

$\mathfrak{O}_j - \mathfrak{O}_k$ partial derivative

The second partial derivative of (12.62) with respect to the orientational parameters \mathfrak{O}_j and \mathfrak{O}_k is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial^2 c_i}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1-S^2)(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right). \quad (12.72)$$

$\mathfrak{O}_j - S^2$ partial derivative

The second partial derivative of (12.62) with respect to the orientational parameter \mathfrak{O}_j and the order parameter S^2 is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial S^2} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i \left(\frac{1}{1 + (\omega \tau_i)^2} - \frac{(\tau_e + \tau_i)\tau_e}{(\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2} \right). \quad (12.73)$$

$\mathfrak{O}_j - \tau_e$ partial derivative

The second partial derivative of (12.62) with respect to the orientational parameter \mathfrak{O}_j and the correlation time τ_e is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial \tau_e} = \frac{2}{5}(1-S^2) \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2}. \quad (12.74)$$

$S^2 - S^2$ partial derivative

The second partial derivative of (12.62) with respect to the order parameter S^2 twice is

$$\frac{\partial^2 J(\omega)}{(\partial S^2)^2} = 0. \quad (12.75)$$

$S^2 - \tau_e$ partial derivative

The second partial derivative of (12.62) with respect to the order parameter S^2 and correlation time τ_e is

$$\frac{\partial^2 J(\omega)}{\partial S^2 \cdot \partial \tau_e} = -\frac{2}{5} \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_e + \tau_i)^2 - (\omega \tau_e \tau_i)^2}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^2}. \quad (12.76)$$

 $\tau_e - \tau_e$ partial derivative

The second partial derivative of (12.62) with respect to the correlation time τ_e twice is

$$\frac{\partial^2 J(\omega)}{\partial \tau_e^2} = -\frac{4}{5}(1 - S^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_e + \tau_i)^3 + 3\omega^2 \tau_i^3 \tau_e (\tau_e + \tau_i) - (\omega \tau_i)^4 \tau_e^3}{((\tau_e + \tau_i)^2 + (\omega \tau_e \tau_i)^2)^3} \quad (12.77)$$

12.8.4 The extended model-free gradient

The model-free gradient of the extended spectral density function (12.63) is the vector of partial derivatives of the function with respect to the geometric parameter \mathfrak{G}_i , the orientational parameter \mathfrak{O}_i , the order parameters S^2 and S_f^2 , and the internal correlation times τ_f and τ_s . The positions in the vector correspond to the model parameters which are being optimised.

\mathfrak{G}_j partial derivative

The partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j is

$$\begin{aligned} \frac{\partial J(\omega)}{\partial \mathfrak{G}_j} = & \frac{2}{5} \sum_{i=-k}^k \left(c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \left(S^2 \frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} \right. \right. \\ & + (1 - S_f^2) \tau_f^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2} \\ & \left. \left. + (S_f^2 - S^2) \tau_s^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \right) \right. \\ & \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right) \right). \quad (12.78) \end{aligned}$$

\mathfrak{O}_j partial derivative

The partial derivative of (12.63) with respect to the orientational parameter \mathfrak{O}_j is

$$\frac{\partial J(\omega)}{\partial \mathfrak{O}_j} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.79)$$

S^2 partial derivative

The partial derivative of (12.63) with respect to the order parameter S^2 is

$$\frac{\partial J(\omega)}{\partial S^2} = \frac{2}{5} \sum_{i=-k}^k c_i \tau_i \left(\frac{1}{1 + (\omega \tau_i)^2} - \frac{(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.80)$$

S_f^2 partial derivative

The partial derivative of (12.63) with respect to the order parameter S_f^2 is

$$\frac{\partial J(\omega)}{\partial S_f^2} = -\frac{2}{5} \sum_{i=-k}^k c_i \tau_i \left(\frac{(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} - \frac{(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.81)$$

τ_f partial derivative

The partial derivative of (12.63) with respect to the correlation time τ_f is

$$\frac{\partial J(\omega)}{\partial \tau_f} = \frac{2}{5}(1 - S_f^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2}. \quad (12.82)$$

 τ_s partial derivative

The partial derivative of (12.63) with respect to the correlation time τ_s is

$$\frac{\partial J(\omega)}{\partial \tau_s} = \frac{2}{5}(S_f^2 - S^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2}. \quad (12.83)$$

12.8.5 The extended model-free Hessian

The model-free Hessian of the extended spectral density function (12.63) is the matrix of second partial derivatives. The matrix coordinates correspond to the model parameters which are being optimised.

$\mathfrak{G}_j - \mathfrak{G}_k$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameters \mathfrak{G}_j and \mathfrak{G}_k is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} = & \frac{2}{5} \sum_{i=-k}^k \left(-2c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \cdot \frac{\partial \tau_i}{\partial \mathfrak{G}_k} \left(S^2 \omega^2 \tau_i \frac{3 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^3} \right. \right. \\ & + (1 - S_f^2) \tau_f^2 \frac{(\tau_f + \tau_i)^3 + 3\omega^2 \tau_f^3 \tau_i (\tau_f + \tau_i) - (\omega \tau_f)^4 \tau_i^3}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^3} \\ & + (S_f^2 - S^2) \tau_s^2 \frac{(\tau_s + \tau_i)^3 + 3\omega^2 \tau_s^3 \tau_i (\tau_s + \tau_i) - (\omega \tau_s)^4 \tau_i^3}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^3} \left. \left. \right) \right. \\ & + \left(\frac{\partial \tau_i}{\partial \mathfrak{G}_j} \cdot \frac{\partial c_i}{\partial \mathfrak{G}_k} + \frac{\partial \tau_i}{\partial \mathfrak{G}_k} \cdot \frac{\partial c_i}{\partial \mathfrak{G}_j} + c_i \frac{\partial^2 \tau_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} \right) \left(S^2 \frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} \right. \\ & + (1 - S_f^2) \tau_f^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2} \\ & + (S_f^2 - S^2) \tau_s^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \left. \right) \\ & + \left(\frac{\partial^2 c_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{G}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right) \right). \end{aligned} \quad (12.84)$$

$\mathfrak{G}_j - \mathfrak{O}_k$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j and the orientational parameter \mathfrak{O}_k is

$$\begin{aligned} \frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{O}_k} = & \frac{2}{5} \sum_{i=-k}^k \left(\frac{\partial \tau_i}{\partial \mathfrak{G}_j} \frac{\partial c_i}{\partial \mathfrak{O}_k} \left(S^2 \frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} \right. \right. \\ & + (1 - S_f^2) \tau_f^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2} \\ & + (S_f^2 - S^2) \tau_s^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \left. \left. \right) \right. \\ & + \frac{\partial^2 c_i}{\partial \mathfrak{G}_j \cdot \partial \mathfrak{O}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right) \right). \end{aligned} \quad (12.85)$$

$\mathfrak{G}_j - S^2$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j and the order parameter S^2 is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial S^2} = \frac{2}{5} \sum_{i=-k}^k \left(c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \left(\frac{1 - (\omega \tau_i)^2}{(1 + (\omega \tau_i)^2)^2} - \tau_s^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \right) \right. \\ \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i \left(\frac{1}{1 + (\omega \tau_i)^2} - \frac{(\tau_s + \tau_i) \tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right) \right). \quad (12.86)$$

$\mathfrak{G}_j - S_f^2$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j and the order parameter S_f^2 is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial S_f^2} = -\frac{2}{5} \sum_{i=-k}^k \left(c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \left(\tau_f^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2} - \tau_s^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \right) \right. \\ \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i \left(\frac{(\tau_f + \tau_i) \tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} - \frac{(\tau_s + \tau_i) \tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right) \right). \quad (12.87)$$

$\mathfrak{G}_j - \tau_f$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j and the correlation time τ_f is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \tau_f} = \frac{2}{5} (1 - S_f^2) \sum_{i=-k}^k \left(2c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \tau_f \tau_i (\tau_f + \tau_i) \frac{(\tau_f + \tau_i)^2 - 3(\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^3} \right. \\ \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2} \right). \quad (12.88)$$

$\mathfrak{G}_j - \tau_s$ partial derivative

The second partial derivative of (12.63) with respect to the geometric parameter \mathfrak{G}_j and the correlation time τ_s is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{G}_j \cdot \partial \tau_s} = \frac{2}{5} (S_f^2 - S^2) \sum_{i=-k}^k \left(2c_i \frac{\partial \tau_i}{\partial \mathfrak{G}_j} \tau_s \tau_i (\tau_s + \tau_i) \frac{(\tau_s + \tau_i)^2 - 3(\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^3} \right. \\ \left. + \frac{\partial c_i}{\partial \mathfrak{G}_j} \tau_i^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2} \right). \quad (12.89)$$

$\mathfrak{O}_j - \mathfrak{O}_k$ partial derivative

The second partial derivative of (12.63) with respect to the orientational parameters \mathfrak{O}_j and \mathfrak{O}_k is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial^2 c_i}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} \tau_i \left(\frac{S^2}{1 + (\omega \tau_i)^2} + \frac{(1 - S_f^2)(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} + \frac{(S_f^2 - S^2)(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.90)$$

$\mathfrak{O}_j - S^2$ partial derivative

The second partial derivative of (12.63) with respect to the orientational parameter \mathfrak{O}_j and the order parameter S^2 is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial S^2} = \frac{2}{5} \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i \left(\frac{1}{1 + (\omega \tau_i)^2} - \frac{(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.91)$$

$\mathfrak{O}_j - S_f^2$ partial derivative

The second partial derivative of (12.63) with respect to the orientational parameter \mathfrak{O}_j and the order parameter S_f^2 is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial S_f^2} = -\frac{2}{5} \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i \left(\frac{(\tau_f + \tau_i)\tau_f}{(\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2} - \frac{(\tau_s + \tau_i)\tau_s}{(\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2} \right). \quad (12.92)$$

$\mathfrak{O}_j - \tau_f$ partial derivative

The second partial derivative of (12.63) with respect to the orientational parameter \mathfrak{O}_j and the correlation time τ_f is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial \tau_f} = \frac{2}{5}(1 - S_f^2) \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2}. \quad (12.93)$$

$\mathfrak{O}_j - \tau_s$ partial derivative

The second partial derivative of (12.63) with respect to the orientational parameter \mathfrak{O}_j and the correlation time τ_s is

$$\frac{\partial^2 J(\omega)}{\partial \mathfrak{O}_j \cdot \partial \tau_s} = \frac{2}{5}(S_f^2 - S^2) \sum_{i=-k}^k \frac{\partial c_i}{\partial \mathfrak{O}_j} \tau_i^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2}. \quad (12.94)$$

$S^2 - S^2$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S^2 twice is

$$\frac{\partial^2 J(\omega)}{(\partial S^2)^2} = 0. \quad (12.95)$$

 $S^2 - S_f^2$ partial derivative

The second partial derivative of (12.63) with respect to the order parameters S^2 and S_f^2 is

$$\frac{\partial^2 J(\omega)}{\partial S^2 \cdot \partial S_f^2} = 0. \quad (12.96)$$

 $S^2 - \tau_f$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S^2 and correlation time τ_f is

$$\frac{\partial^2 J(\omega)}{\partial S^2 \cdot \partial \tau_f} = 0. \quad (12.97)$$

 $S^2 - \tau_s$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S^2 and correlation time τ_s is

$$\frac{\partial^2 J(\omega)}{\partial S^2 \cdot \partial \tau_s} = -\frac{2}{5} \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2}. \quad (12.98)$$

 $S_f^2 - S_f^2$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S_f^2 twice is

$$\frac{\partial^2 J(\omega)}{(\partial S_f^2)^2} = 0. \quad (12.99)$$

 $S_f^2 - \tau_f$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S_f^2 and correlation time τ_f is

$$\frac{\partial^2 J(\omega)}{\partial S_f^2 \cdot \partial \tau_f} = -\frac{2}{5} \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_f + \tau_i)^2 - (\omega \tau_f \tau_i)^2}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^2}. \quad (12.100)$$

$S_f^2 - \tau_s$ partial derivative

The second partial derivative of (12.63) with respect to the order parameter S_f^2 and correlation time τ_s is

$$\frac{\partial^2 J(\omega)}{\partial S_f^2 \cdot \partial \tau_s} = \frac{2}{5} \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_s + \tau_i)^2 - (\omega \tau_s \tau_i)^2}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^2}. \quad (12.101)$$

 $\tau_f - \tau_f$ partial derivative

The second partial derivative of (12.62) with respect to the correlation time τ_f twice is

$$\frac{\partial^2 J(\omega)}{\partial \tau_f^2} = -\frac{4}{5}(1 - S_f^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_f + \tau_i)^3 + 3\omega^2 \tau_i^3 \tau_f (\tau_f + \tau_i) - (\omega \tau_i)^4 \tau_f^3}{((\tau_f + \tau_i)^2 + (\omega \tau_f \tau_i)^2)^3} \quad (12.102)$$

 $\tau_f - \tau_s$ partial derivative

The second partial derivative of (12.62) with respect to the correlation times τ_f and τ_s is

$$\frac{\partial^2 J(\omega)}{\partial \tau_f \cdot \partial \tau_s} = 0. \quad (12.103)$$

 $\tau_s - \tau_s$ partial derivative

The second partial derivative of (12.62) with respect to the correlation time τ_s twice is

$$\frac{\partial^2 J(\omega)}{\partial \tau_s^2} = -\frac{4}{5}(S_f^2 - S^2) \sum_{i=-k}^k c_i \tau_i^2 \frac{(\tau_s + \tau_i)^3 + 3\omega^2 \tau_i^3 \tau_s (\tau_s + \tau_i) - (\omega \tau_i)^4 \tau_s^3}{((\tau_s + \tau_i)^2 + (\omega \tau_s \tau_i)^2)^3} \quad (12.104)$$

12.9 Ellipsoidal diffusion tensor

12.9.1 The diffusion equation of the ellipsoid

The correlation function of the Brownian rotational diffusion of an ellipsoid is

$$C_O(\tau) = \frac{1}{5} \sum_{i=-2}^2 c_i e^{-\frac{\tau}{\tau_i}}. \quad (12.105)$$

where c_i are the weights of the five exponential terms which are dependent on the orientation of the XH bond vector and τ_i are the correlation times of the five exponential terms.

12.9.2 The weights of the ellipsoid

Definitions

The three direction cosines defining the XH bond vector within the diffusion frame are

$$\delta_x = \widehat{XH} \cdot \widehat{\mathfrak{D}}_x, \quad (12.106a)$$

$$\delta_y = \widehat{XH} \cdot \widehat{\mathfrak{D}}_y, \quad (12.106b)$$

$$\delta_z = \widehat{XH} \cdot \widehat{\mathfrak{D}}_z. \quad (12.106c)$$

Let the set of geometric parameters be

$$\mathfrak{G} = \{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r\}, \quad (12.107)$$

and the set of orientational parameters be the Euler angles

$$\mathfrak{O} = \{\alpha, \beta, \gamma\}. \quad (12.108)$$

The weights

The five weights c_i in the correlation function of the Brownian rotational diffusion of an ellipsoid (12.105) are

$$c_{-2} = \frac{1}{4}(d - e), \quad (12.109a)$$

$$c_{-1} = 3\delta_y^2 \delta_z^2, \quad (12.109b)$$

$$c_0 = 3\delta_x^2 \delta_z^2, \quad (12.109c)$$

$$c_1 = 3\delta_x^2 \delta_y^2, \quad (12.109d)$$

$$c_2 = \frac{1}{4}(d + e), \quad (12.109e)$$

where

$$d = 3(\delta_x^4 + \delta_y^4 + \delta_z^4) - 1, \quad (12.110)$$

$$e = \frac{1}{\mathfrak{R}} \left[(1 + 3\mathfrak{D}_r) (\delta_x^4 + 2\delta_y^2\delta_z^2) + (1 - 3\mathfrak{D}_r) (\delta_y^4 + 2\delta_x^2\delta_z^2) - 2(\delta_z^4 + 2\delta_x^2\delta_y^2) \right]. \quad (12.111)$$

The factor \mathfrak{R} is defined as

$$\mathfrak{R} = \sqrt{1 + 3\mathfrak{D}_r^2}. \quad (12.112)$$

12.9.3 The weight gradients of the ellipsoid

\mathfrak{O}_i partial derivative

The partial derivatives with respect to the orientational parameter \mathfrak{O}_i are

$$\frac{\partial c_{-2}}{\partial \mathfrak{O}_i} = 3 \left(\delta_x^3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} + \delta_y^3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_z^3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \right) - \frac{\partial e}{\partial \mathfrak{O}_i}, \quad (12.113a)$$

$$\frac{\partial c_{-1}}{\partial \mathfrak{O}_i} = 6\delta_y\delta_z \left(\delta_y \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \right), \quad (12.113b)$$

$$\frac{\partial c_0}{\partial \mathfrak{O}_i} = 6\delta_x\delta_z \left(\delta_x \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right), \quad (12.113c)$$

$$\frac{\partial c_1}{\partial \mathfrak{O}_i} = 6\delta_x\delta_y \left(\delta_x \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_y \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right), \quad (12.113d)$$

$$\frac{\partial c_2}{\partial \mathfrak{O}_i} = 3 \left(\delta_x^3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} + \delta_y^3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_z^3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \right) + \frac{\partial e}{\partial \mathfrak{O}_i}, \quad (12.113e)$$

where

$$\begin{aligned} \frac{\partial e}{\partial \mathfrak{O}_i} = & \frac{1}{\mathfrak{R}} \left[(1 + 3\mathfrak{D}_r) \left(\delta_x^3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} + \delta_y \delta_z \left(\delta_y \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \right) \right) \right. \\ & + (1 - 3\mathfrak{D}_r) \left(\delta_y^3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_x \delta_z \left(\delta_x \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right) \right) \\ & \left. - 2 \left(\delta_z^3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_x \delta_y \left(\delta_x \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_y \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right) \right) \right]. \end{aligned} \quad (12.114)$$

τ_m partial derivative

The partial derivatives with respect to the τ_m geometric parameter are

$$\frac{\partial c_{-2}}{\partial \tau_m} = 0, \quad (12.115a)$$

$$\frac{\partial c_{-1}}{\partial \tau_m} = 0, \quad (12.115b)$$

$$\frac{\partial c_0}{\partial \tau_m} = 0, \quad (12.115c)$$

$$\frac{\partial c_1}{\partial \tau_m} = 0, \quad (12.115d)$$

$$\frac{\partial c_2}{\partial \tau_m} = 0. \quad (12.115e)$$

 \mathfrak{D}_a partial derivative

The partial derivatives with respect to the \mathfrak{D}_a geometric parameter are

$$\frac{\partial c_{-2}}{\partial \mathfrak{D}_a} = 0, \quad (12.116a)$$

$$\frac{\partial c_{-1}}{\partial \mathfrak{D}_a} = 0, \quad (12.116b)$$

$$\frac{\partial c_0}{\partial \mathfrak{D}_a} = 0, \quad (12.116c)$$

$$\frac{\partial c_1}{\partial \mathfrak{D}_a} = 0, \quad (12.116d)$$

$$\frac{\partial c_2}{\partial \mathfrak{D}_a} = 0. \quad (12.116e)$$

 \mathfrak{D}_r partial derivative

The partial derivatives with respect to the \mathfrak{D}_r geometric parameter are

$$\frac{\partial c_{-2}}{\partial \mathfrak{D}_r} = -\frac{3}{4} \frac{\partial e}{\partial \mathfrak{D}_r}, \quad (12.117a)$$

$$\frac{\partial c_{-1}}{\partial \mathfrak{D}_r} = 0, \quad (12.117b)$$

$$\frac{\partial c_0}{\partial \mathfrak{D}_r} = 0, \quad (12.117c)$$

$$\frac{\partial c_1}{\partial \mathfrak{D}_r} = 0, \quad (12.117d)$$

$$\frac{\partial c_2}{\partial \mathfrak{D}_r} = \frac{3}{4} \frac{\partial e}{\partial \mathfrak{D}_r}, \quad (12.117e)$$

where

$$\frac{\partial e}{\partial \mathfrak{D}_r} = \frac{1}{\mathfrak{R}^3} \left[(1 - \mathfrak{D}_r) (\delta_x^4 + 2\delta_y^2\delta_z^2) - (1 + \mathfrak{D}_r) (\delta_y^4 + 2\delta_x^2\delta_z^2) + 2\mathfrak{D}_r (\delta_z^4 + 2\delta_x^2\delta_y^2) \right]. \quad (12.118)$$

12.9.4 The weight Hessians of the ellipsoid

$\mathfrak{O}_i - \mathfrak{O}_j$ partial derivative

The second partial derivatives with respect to the orientational parameters \mathfrak{O}_i and \mathfrak{O}_j are

$$\begin{aligned} \frac{\partial^2 c_{-2}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = & 3 \left(\delta_x^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right) \right. \\ & + \delta_y^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} \right) \\ & \left. + \delta_z^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} \right) \right) - \frac{\partial^2 e}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j}, \end{aligned} \quad (12.119a)$$

$$\begin{aligned} \frac{\partial^2 c_{-1}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = & 6 \delta_y^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} \right) \\ & + 12 \delta_y \delta_z \left(\frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} + \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} \right) \\ & + 6 \delta_z^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} \right), \end{aligned} \quad (12.119b)$$

$$\begin{aligned} \frac{\partial^2 c_0}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = & 6 \delta_x^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} \right) \\ & + 12 \delta_x \delta_z \left(\frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} + \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right) \\ & + 6 \delta_z^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right), \end{aligned} \quad (12.119c)$$

$$\begin{aligned} \frac{\partial^2 c_1}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = & 6 \delta_x^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} \right) \\ & + 12 \delta_x \delta_y \left(\frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} + \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right) \\ & + 6 \delta_y^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right), \end{aligned} \quad (12.119d)$$

$$\begin{aligned} \frac{\partial^2 c_2}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = & 3 \left(\delta_x^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{O}_j} \right) \right. \\ & + \delta_y^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{O}_j} \right) \\ & \left. + \delta_z^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} + 3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} \right) \right) + \frac{\partial^2 e}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j}, \end{aligned} \quad (12.119e)$$

where

$$\begin{aligned}
\frac{\partial^2 e}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} = & \frac{1}{\mathfrak{R}} \left[(1 + 3\mathfrak{D}_r) \left(\delta_x^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + 3 \frac{\partial \delta_x}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{D}_j} \right) \right. \right. \\
& + \delta_y^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_z}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{D}_j} \right) \\
& + \delta_z^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_y}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{D}_j} \right) \\
& \left. \left. + 2\delta_y \delta_z \left(\frac{\partial \delta_y}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{D}_j} + \frac{\partial \delta_z}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{D}_j} \right) \right) \right) \\
& + (1 - 3\mathfrak{D}_r) \left(\delta_y^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + 3 \frac{\partial \delta_y}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{D}_j} \right) \right. \\
& + \delta_x^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_z}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{D}_j} \right) \\
& + \delta_z^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_x}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{D}_j} \right) \\
& \left. \left. + 2\delta_x \delta_z \left(\frac{\partial \delta_x}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{D}_j} + \frac{\partial \delta_z}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{D}_j} \right) \right) \right) \\
& - 2 \left(\delta_z^2 \left(\delta_z \frac{\partial^2 \delta_z}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + 3 \frac{\partial \delta_z}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{D}_j} \right) \right. \\
& + \delta_x^2 \left(\delta_y \frac{\partial^2 \delta_y}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_y}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{D}_j} \right) \\
& + \delta_y^2 \left(\delta_x \frac{\partial^2 \delta_x}{\partial \mathfrak{D}_i \cdot \partial \mathfrak{D}_j} + \frac{\partial \delta_x}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{D}_j} \right) \\
& \left. \left. + 2\delta_x \delta_y \left(\frac{\partial \delta_x}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_y}{\partial \mathfrak{D}_j} + \frac{\partial \delta_y}{\partial \mathfrak{D}_i} \cdot \frac{\partial \delta_x}{\partial \mathfrak{D}_j} \right) \right) \right]. \quad (12.120)
\end{aligned}$$

$\mathfrak{D}_i - \tau_m$ partial derivative

The second partial derivatives with respect to the orientational parameter \mathfrak{D}_i and the geometric parameter τ_m are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{D}_i \cdot \partial \tau_m} = 0, \quad (12.121a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{D}_i \cdot \partial \tau_m} = 0, \quad (12.121b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{D}_i \cdot \partial \tau_m} = 0, \quad (12.121c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{D}_i \cdot \partial \tau_m} = 0, \quad (12.121d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{O}_i \cdot \partial \tau_m} = 0. \quad (12.121e)$$

 $\mathfrak{O}_i - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the orientational parameter \mathfrak{O}_i and the geometric parameter \mathfrak{D}_a are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_a} = 0, \quad (12.122a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_a} = 0, \quad (12.122b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_a} = 0, \quad (12.122c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_a} = 0, \quad (12.122d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_a} = 0. \quad (12.122e)$$

 $O_i - D_r$ partial derivative

The second partial derivatives with respect to the orientational parameter \mathfrak{O}_i and the geometric parameter \mathfrak{D}_r are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = -3 \frac{\partial^2 e}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r}, \quad (12.123a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = 0, \quad (12.123b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = 0, \quad (12.123c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = 0, \quad (12.123d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = 3 \frac{\partial^2 e}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r}, \quad (12.123e)$$

where

$$\begin{aligned} \frac{\partial^2 e}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{D}_r} = & \frac{1}{\mathfrak{R}^3} \left[\left((1 - \mathfrak{D}_r) \left(\delta_x^3 \frac{\partial \delta_x}{\partial \mathfrak{O}_i} + \delta_y \delta_z \left(\delta_y \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_y}{\partial \mathfrak{O}_i} \right) \right) \right. \right. \\ & - (1 + \mathfrak{D}_r) \left(\delta_y^3 \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_x \delta_z \left(\delta_x \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_z \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right) \right) \\ & \left. \left. + 2\mathfrak{D}_r \left(\delta_z^3 \frac{\partial \delta_z}{\partial \mathfrak{O}_i} + \delta_x \delta_y \left(\delta_x \frac{\partial \delta_y}{\partial \mathfrak{O}_i} + \delta_y \frac{\partial \delta_x}{\partial \mathfrak{O}_i} \right) \right) \right] \right]. \end{aligned} \quad (12.124)$$

$\tau_m - \tau_m$ partial derivative

The second partial derivatives with respect to the geometric parameter τ_m twice are

$$\frac{\partial^2 c_{-2}}{\partial \tau_m^2} = 0, \quad (12.125a)$$

$$\frac{\partial^2 c_{-1}}{\partial \tau_m^2} = 0, \quad (12.125b)$$

$$\frac{\partial^2 c_0}{\partial \tau_m^2} = 0, \quad (12.125c)$$

$$\frac{\partial^2 c_1}{\partial \tau_m^2} = 0, \quad (12.125d)$$

$$\frac{\partial^2 c_2}{\partial \tau_m^2} = 0. \quad (12.125e)$$

 $\tau_m - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameters τ_m and \mathfrak{D}_a are

$$\frac{\partial^2 c_{-2}}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 0, \quad (12.126a)$$

$$\frac{\partial^2 c_{-1}}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 0, \quad (12.126b)$$

$$\frac{\partial^2 c_0}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 0, \quad (12.126c)$$

$$\frac{\partial^2 c_1}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 0, \quad (12.126d)$$

$$\frac{\partial^2 c_2}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 0. \quad (12.126e)$$

 $\tau_m - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameters τ_m and \mathfrak{D}_r are

$$\frac{\partial^2 c_{-2}}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0, \quad (12.127a)$$

$$\frac{\partial^2 c_{-1}}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0, \quad (12.127b)$$

$$\frac{\partial^2 c_0}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0, \quad (12.127c)$$

$$\frac{\partial^2 c_1}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0, \quad (12.127d)$$

$$\frac{\partial^2 c_2}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0. \quad (12.127e)$$

$\mathfrak{D}_a - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameter \mathfrak{D}_a twice are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{D}_a^2} = 0, \quad (12.128a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{D}_a^2} = 0, \quad (12.128b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{D}_a^2} = 0, \quad (12.128c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{D}_a^2} = 0, \quad (12.128d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{D}_a^2} = 0. \quad (12.128e)$$

 $\mathfrak{D}_a - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameters \mathfrak{D}_a and \mathfrak{D}_r are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0, \quad (12.129a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0, \quad (12.129b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0, \quad (12.129c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0, \quad (12.129d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0. \quad (12.129e)$$

 $\mathfrak{D}_r - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameter \mathfrak{D}_r twice are

$$\frac{\partial^2 c_{-2}}{\partial \mathfrak{D}_r^2} = -\frac{3}{4} \frac{\partial^2 e}{\partial \mathfrak{D}_r^2}, \quad (12.130a)$$

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{D}_r^2} = 0, \quad (12.130b)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{D}_r^2} = 0, \quad (12.130c)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{D}_r^2} = 0, \quad (12.130d)$$

$$\frac{\partial^2 c_2}{\partial \mathfrak{D}_r^2} = \frac{3}{4} \frac{\partial^2 e}{\partial \mathfrak{D}_r^2}, \quad (12.130e)$$

where

$$\begin{aligned} \frac{\partial^2 e}{\partial \mathfrak{D}_r^2} = \frac{1}{\mathfrak{R}^5} & \left[(6\mathfrak{D}_r^2 - 9\mathfrak{D}_r - 1) (\delta_x^4 + 2\delta_y^2\delta_z^2) \right. \\ & + (6\mathfrak{D}_r^2 + 9\mathfrak{D}_r - 1) (\delta_y^4 + 2\delta_x^2\delta_z^2) \\ & \left. - 2(6\mathfrak{D}_r^2 - 1) (\delta_z^4 + 2\delta_x^2\delta_y^2) \right]. \end{aligned} \quad (12.131)$$

12.9.5 The correlation times of the ellipsoid

The five correlation times τ_i in the correlation function of the Brownian rotational diffusion of an ellipsoid (12.105) on page 205 are

$$\tau_{-2} = (6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-1}, \quad (12.132a)$$

$$\tau_{-1} = (6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-1}, \quad (12.132b)$$

$$\tau_0 = (6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-1}, \quad (12.132c)$$

$$\tau_1 = (6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-1}, \quad (12.132d)$$

$$\tau_2 = (6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-1}, \quad (12.132e)$$

where \mathfrak{R} is defined in Equation (12.112) on page 206.

12.9.6 The correlation time gradients of the ellipsoid

τ_m partial derivative

The partial derivatives with respect to the geometric parameter τ_m are

$$\frac{\partial \tau_{-2}}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-2}, \quad (12.133a)$$

$$\frac{\partial \tau_{-1}}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-2}, \quad (12.133b)$$

$$\frac{\partial \tau_0}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-2}, \quad (12.133c)$$

$$\frac{\partial \tau_1}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}, \quad (12.133d)$$

$$\frac{\partial \tau_2}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-2}. \quad (12.133e)$$

\mathfrak{D}_a partial derivative

The partial derivatives with respect to the geometric parameter \mathfrak{D}_a are

$$\frac{\partial \tau_{-2}}{\partial \mathfrak{D}_a} = 2\mathfrak{R}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-2}, \quad (12.134a)$$

$$\frac{\partial \tau_{-1}}{\partial \mathfrak{D}_a} = (1 + 3\mathfrak{D}_r)(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-2}, \quad (12.134b)$$

$$\frac{\partial \tau_0}{\partial \mathfrak{D}_a} = (1 - 3\mathfrak{D}_r)(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-2}, \quad (12.134c)$$

$$\frac{\partial \tau_1}{\partial \mathfrak{D}_a} = -2(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}, \quad (12.134d)$$

$$\frac{\partial \tau_2}{\partial \mathfrak{D}_a} = -2\mathfrak{R}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-2}. \quad (12.134e)$$

\mathfrak{D}_r partial derivative

The partial derivatives with respect to the geometric parameter \mathfrak{D}_r are

$$\frac{\partial \tau_{-2}}{\partial \mathfrak{D}_r} = 6 \frac{\mathfrak{D}_a \mathfrak{D}_r}{\mathfrak{R}} (6\mathfrak{D}_{iso} - 2\mathfrak{D}_a \mathfrak{R})^{-2}, \quad (12.135a)$$

$$\frac{\partial \tau_{-1}}{\partial \mathfrak{D}_r} = 3\mathfrak{D}_a (6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-2}, \quad (12.135b)$$

$$\frac{\partial \tau_0}{\partial \mathfrak{D}_r} = -3\mathfrak{D}_a (6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-2}, \quad (12.135c)$$

$$\frac{\partial \tau_1}{\partial \mathfrak{D}_r} = 0, \quad (12.135d)$$

$$\frac{\partial \tau_2}{\partial \mathfrak{D}_r} = -6 \frac{\mathfrak{D}_a \mathfrak{D}_r}{\mathfrak{R}} (6\mathfrak{D}_{iso} + 2\mathfrak{D}_a \mathfrak{R})^{-2}. \quad (12.135e)$$

12.9.7 The correlation time Hessians of the ellipsoid

$\tau_m - \tau_m$ partial derivative

The second partial derivatives with respect to the geometric parameter τ_m twice are

$$\frac{\partial^2 \tau_{-2}}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-2}, \quad (12.136a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-2}, \quad (12.136b)$$

$$\frac{\partial^2 \tau_0}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-2}, \quad (12.136c)$$

$$\frac{\partial^2 \tau_1}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}, \quad (12.136d)$$

$$\frac{\partial^2 \tau_2}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-2}. \quad (12.136e)$$

$\tau_m - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameters τ_m and \mathfrak{D}_a are

$$\frac{\partial^2 \tau_{-2}}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 4\mathfrak{R}\tau_m^{-2}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3}, \quad (12.137a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 2(1 + 3\mathfrak{D}_r)\tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3}, \quad (12.137b)$$

$$\frac{\partial^2 \tau_0}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 2(1 - 3\mathfrak{D}_r)\tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3}, \quad (12.137c)$$

$$\frac{\partial^2 \tau_1}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = -4\tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3}, \quad (12.137d)$$

$$\frac{\partial^2 \tau_2}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = -4\mathfrak{R}\tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-3}. \quad (12.137e)$$

$\tau_m - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameters τ_m and \mathfrak{D}_r are

$$\frac{\partial^2 \tau_{-2}}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 12\frac{\mathfrak{D}_a\mathfrak{D}_r}{\mathfrak{R}}\tau_m^{-2}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3}, \quad (12.138a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 6\mathfrak{D}_a\tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3}, \quad (12.138b)$$

$$\frac{\partial^2 \tau_0}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = -6\mathfrak{D}_a\tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3}, \quad (12.138c)$$

$$\frac{\partial^2 \tau_1}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = 0, \quad (12.138d)$$

$$\frac{\partial^2 \tau_2}{\partial \tau_m \cdot \partial \mathfrak{D}_r} = -12\frac{\mathfrak{D}_a\mathfrak{D}_r}{\mathfrak{R}}\tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-3}. \quad (12.138e)$$

$\mathfrak{D}_a - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameter \mathfrak{D}_a twice are

$$\frac{\partial^2 \tau_{-2}}{\partial \mathfrak{D}_a^2} = 8\mathfrak{R}^2(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3}, \quad (12.139a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \mathfrak{D}_a^2} = 2(1 + 3\mathfrak{D}_r)^2(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3}, \quad (12.139b)$$

$$\frac{\partial^2 \tau_0}{\partial \mathfrak{D}_a^2} = 2(1 - 3\mathfrak{D}_r)^2(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3}, \quad (12.139c)$$

$$\frac{\partial^2 \tau_1}{\partial \mathfrak{D}_a^2} = 8(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3}, \quad (12.139d)$$

$$\frac{\partial^2 \tau_2}{\partial \mathfrak{D}_a^2} = 8\mathfrak{R}^2(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-3}. \quad (12.139e)$$

 $\mathfrak{D}_a - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameters \mathfrak{D}_a and \mathfrak{D}_r are

$$\frac{\partial^2 \tau_{-2}}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 24\mathfrak{D}_a\mathfrak{D}_r(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3} + 6\frac{\mathfrak{D}_r}{\mathfrak{R}}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-2}, \quad (12.140a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 6\mathfrak{D}_a(1 + 3\mathfrak{D}_r)(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3} + 3(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-2}, \quad (12.140b)$$

$$\frac{\partial^2 \tau_0}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = -6\mathfrak{D}_a(1 - 3\mathfrak{D}_r)(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3} - 3(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-2}, \quad (12.140c)$$

$$\frac{\partial^2 \tau_1}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 0, \quad (12.140d)$$

$$\frac{\partial^2 \tau_2}{\partial \mathfrak{D}_a \cdot \partial \mathfrak{D}_r} = 24\mathfrak{D}_a\mathfrak{D}_r(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-3} - 6\frac{\mathfrak{D}_r}{\mathfrak{R}}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-2}. \quad (12.140e)$$

 $\mathfrak{D}_r - \mathfrak{D}_r$ partial derivative

The second partial derivatives with respect to the geometric parameter \mathfrak{D}_r twice are

$$\frac{\partial^2 \tau_{-2}}{\partial \mathfrak{D}_r^2} = 72 \left(\frac{\mathfrak{D}_a \mathfrak{D}_r}{\mathfrak{R}} \right)^2 (6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3} + 6\frac{\mathfrak{D}_a}{\mathfrak{R}^3}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-2}, \quad (12.141a)$$

$$\frac{\partial^2 \tau_{-1}}{\partial \mathfrak{D}_r^2} = 18\mathfrak{D}_a^2(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 + 3\mathfrak{D}_r))^{-3}, \quad (12.141b)$$

$$\frac{\partial^2 \tau_0}{\partial \mathfrak{D}_r^2} = 18\mathfrak{D}_a^2(6\mathfrak{D}_{iso} - \mathfrak{D}_a(1 - 3\mathfrak{D}_r))^{-3}, \quad (12.141c)$$

$$\frac{\partial^2 \tau_1}{\partial \mathfrak{D}_r^2} = 0, \quad (12.141d)$$

$$\frac{\partial^2 \tau_2}{\partial \mathfrak{D}_r^2} = 72 \left(\frac{\mathfrak{D}_a \mathfrak{D}_r}{\mathfrak{R}} \right)^2 (6\mathfrak{D}_{iso} - 2\mathfrak{D}_a\mathfrak{R})^{-3} - 6\frac{\mathfrak{D}_a}{\mathfrak{R}^3}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a\mathfrak{R})^{-2}. \quad (12.141e)$$

12.10 Spheroidal diffusion tensor

12.10.1 The diffusion equation of the spheroid

The correlation function of the Brownian rotational diffusion of a spheroid is

$$C_O(\tau) = \frac{1}{5} \sum_{i=-1}^1 c_i e^{-\frac{\tau}{\tau_i}}. \quad (12.142)$$

where c_i are the weights of the three exponential terms which are dependent on the orientation of the XH bond vector and τ_i are the correlation times of the three exponential terms.

12.10.2 The weights of the spheroid

Definitions

The direction cosine defining the XH bond vector within the spheroidal diffusion frame is

$$\delta_z = \widehat{XH} \cdot \widehat{\mathfrak{D}_z}. \quad (12.143)$$

Let the set of geometric parameters be

$$\mathfrak{G} = \{\mathfrak{D}_{iso}, \mathfrak{D}_a\}, \quad (12.144)$$

and the set of orientational parameters be the spherical angles

$$\mathfrak{O} = \{\theta, \phi\}. \quad (12.145)$$

The weights

The three spheroid weights c_i in the correlation function of the Brownian rotational diffusion of a spheroid (12.142) are

$$c_{-1} = \frac{1}{4}(3\delta_z^2 - 1)^2, \quad (12.146a)$$

$$c_0 = 3\delta_z^2(1 - \delta_z^2), \quad (12.146b)$$

$$c_1 = \frac{3}{4}(\delta_z^2 - 1)^2. \quad (12.146c)$$

12.10.3 The weight gradients of the spheroid

\mathfrak{O}_i partial derivative

The partial derivatives with respect to the orientational parameter \mathfrak{O}_i are

$$\frac{\partial c_{-1}}{\partial \mathfrak{O}_i} = 3\delta_z(3\delta_z^2 - 1)\frac{\partial \delta_z}{\partial \mathfrak{O}_i}, \quad (12.147a)$$

$$\frac{\partial c_0}{\partial \mathfrak{O}_i} = 6\delta_z(1 - 2\delta_z^2)\frac{\partial \delta_z}{\partial \mathfrak{O}_i}, \quad (12.147b)$$

$$\frac{\partial c_1}{\partial \mathfrak{O}_i} = 3\delta_z(\delta_z^2 - 1)\frac{\partial \delta_z}{\partial \mathfrak{O}_i}. \quad (12.147c)$$

12.10.4 The weight Hessians of the spheroid

$\mathfrak{O}_i - \mathfrak{O}_j$ partial derivative

The second partial derivatives with respect to the orientational parameters \mathfrak{O}_i and \mathfrak{O}_j are

$$\frac{\partial^2 c_{-1}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = 3 \left((9\delta_z^2 - 1) \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} + \delta_z(3\delta_z^2 - 1) \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} \right), \quad (12.148a)$$

$$\frac{\partial^2 c_0}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = 6 \left((1 - 6\delta_z^2) \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} + \delta_z(1 - 2\delta_z^2) \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} \right), \quad (12.148b)$$

$$\frac{\partial^2 c_1}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = 3 \left((3\delta_z^2 - 1) \frac{\partial \delta_z}{\partial \mathfrak{O}_i} \cdot \frac{\partial \delta_z}{\partial \mathfrak{O}_j} + \delta_z(\delta_z^2 - 1) \frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} \right). \quad (12.148c)$$

12.10.5 The correlation times of the spheroid

The three spheroid correlation times τ_i in the correlation function of the Brownian rotational diffusion of a spheroid (12.142) are

$$\tau_{-1} = (6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-1}, \quad (12.149a)$$

$$\tau_0 = (6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-1}, \quad (12.149b)$$

$$\tau_1 = (6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-1}. \quad (12.149c)$$

12.10.6 The correlation time gradients of the spheroid

τ_m partial derivative

The partial derivatives with respect to the geometric parameter τ_m are

$$\frac{\partial \tau_{-1}}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-2}, \quad (12.150a)$$

$$\frac{\partial \tau_0}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-2}, \quad (12.150b)$$

$$\frac{\partial \tau_1}{\partial \tau_m} = \tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}. \quad (12.150c)$$

\mathfrak{D}_a partial derivative

The partial derivatives with respect to the geometric parameter \mathfrak{D}_a are

$$\frac{\partial \tau_{-1}}{\partial \mathfrak{D}_a} = 2(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-2}, \quad (12.151a)$$

$$\frac{\partial \tau_0}{\partial \mathfrak{D}_a} = (6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-2}, \quad (12.151b)$$

$$\frac{\partial \tau_1}{\partial \mathfrak{D}_a} = -2(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}. \quad (12.151c)$$

12.10.7 The correlation time Hessians of the spheroid

$\tau_m - \tau_m$ partial derivative

The second partial derivatives with respect to the geometric parameter τ_m twice are

$$\frac{\partial^2 \tau_{-1}}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-2}, \quad (12.152a)$$

$$\frac{\partial^2 \tau_0}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-2}, \quad (12.152b)$$

$$\frac{\partial^2 \tau_1}{\partial \tau_m^2} = 2\tau_m^{-4}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3} - 2\tau_m^{-3}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-2}. \quad (12.152c)$$

$\tau_m - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameters τ_m and \mathfrak{D}_a are

$$\frac{\partial^2 \tau_{-1}}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 4\tau_m^{-2}(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-3}, \quad (12.153a)$$

$$\frac{\partial^2 \tau_0}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = 2\tau_m^{-2}(6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-3}, \quad (12.153b)$$

$$\frac{\partial^2 \tau_1}{\partial \tau_m \cdot \partial \mathfrak{D}_a} = -4\tau_m^{-2}(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3}. \quad (12.153c)$$

 $\mathfrak{D}_a - \mathfrak{D}_a$ partial derivative

The second partial derivatives with respect to the geometric parameter \mathfrak{D}_a twice are

$$\frac{\partial^2 \tau_{-1}}{\partial \mathfrak{D}_a^2} = 8(6\mathfrak{D}_{iso} - 2\mathfrak{D}_a)^{-3}, \quad (12.154a)$$

$$\frac{\partial^2 \tau_0}{\partial \mathfrak{D}_a^2} = 2(6\mathfrak{D}_{iso} - \mathfrak{D}_a)^{-3}, \quad (12.154b)$$

$$\frac{\partial^2 \tau_1}{\partial \mathfrak{D}_a^2} = 8(6\mathfrak{D}_{iso} + 2\mathfrak{D}_a)^{-3}. \quad (12.154c)$$

12.11 Spherical diffusion tensor

12.11.1 The diffusion equation of the sphere

The correlation function of the Brownian rotational diffusion of a sphere is

$$C_O(\tau) = \frac{1}{5} e^{-\frac{\tau}{\tau_m}}, \quad (12.155)$$

$$= \frac{1}{5} \sum_{i=0}^0 c_i e^{-\frac{\tau}{\tau_i}}. \quad (12.156)$$

where c_i is the weight of the single exponential term and τ_i is the correlation time of the single exponential term.

12.11.2 The weight of the sphere

Definitions

The entire diffusion parameter set consists of a single geometric parameter and is

$$\mathfrak{D} = \{\tau_m\}. \quad (12.157)$$

Summation terms

The summation indices of the correlation function of the Brownian rotational diffusion of a sphere (12.142) range from $k = 0$ to $k = 0$ therefore

$$i \in \{0\}. \quad (12.158)$$

The weights

The single weight c_i in the correlation function of the Brownian rotational diffusion of a sphere (12.142) is

$$c_0 = 1. \quad (12.159)$$

12.11.3 The weight gradient of the sphere

τ_m partial derivative

The partial derivative with respect to the geometric parameter τ_m is

$$\frac{\partial c_0}{\partial \tau_m} = 0. \quad (12.160)$$

12.11.4 The weight Hessian of the sphere

$\tau_m - \tau_m$ partial derivative

The second partial derivatives with respect to the geometric parameter τ_m twice is

$$\frac{\partial^2 c_0}{\partial \tau_m^2} = 0. \quad (12.161)$$

12.11.5 The correlation time of the sphere

The single correlation time τ_i of the correlation function of the Brownian rotational diffusion of a sphere (12.142) is

$$\tau_0 = \tau_m. \quad (12.162)$$

12.11.6 The correlation time gradient of the sphere

τ_m partial derivative

The partial derivative with respect to the geometric parameter τ_m is

$$\frac{\partial \tau_0}{\partial \tau_m} = 1. \quad (12.163)$$

12.11.7 The correlation time Hessian of the sphere

$\tau_m - \tau_m$ partial derivative

The second partial derivative with respect to the geometric parameter τ_m twice is

$$\frac{\partial^2 \tau_0}{\partial \tau_m^2} = 0. \quad (12.164)$$

12.12 Ellipsoidal dot product derivatives

12.12.1 The dot product of the ellipsoid

The dot product is defined as

$$\delta_i = \widehat{XH} \cdot \widehat{\mathfrak{D}}_i, \quad (12.165)$$

where i is one of $\{x, y, z\}$, \widehat{XH} is a unit vector parallel to the XH bond vector, and $\widehat{\mathfrak{D}}_i$ is one of the unit vectors defining the diffusion frame. The three diffusion frame unit vectors can be expressed using the Euler angles α , β , and γ as

$$\widehat{\mathfrak{D}}_x = \begin{pmatrix} -\sin \alpha \sin \gamma + \cos \alpha \cos \beta \cos \gamma \\ -\sin \alpha \cos \gamma - \cos \alpha \cos \beta \sin \gamma \\ \cos \alpha \sin \beta \end{pmatrix}, \quad (12.166a)$$

$$\widehat{\mathfrak{D}}_y = \begin{pmatrix} \cos \alpha \sin \gamma + \sin \alpha \cos \beta \cos \gamma \\ \cos \alpha \cos \gamma - \sin \alpha \cos \beta \sin \gamma \\ \sin \alpha \sin \beta \end{pmatrix}, \quad (12.166b)$$

$$\widehat{\mathfrak{D}}_z = \begin{pmatrix} -\sin \beta \cos \gamma \\ \sin \beta \sin \gamma \\ \cos \beta \end{pmatrix}. \quad (12.166c)$$

12.12.2 The dot product gradient of the ellipsoid

The partial derivative of the dot product δ_i with respect to the orientational parameter \mathfrak{D}_j is

$$\frac{\partial \delta_i}{\partial \mathfrak{D}_j} = \frac{\partial}{\partial \mathfrak{D}_j} (\widehat{XH} \cdot \widehat{\mathfrak{D}}_i) = \widehat{XH} \frac{\partial \widehat{\mathfrak{D}}_i}{\partial \mathfrak{D}_j} + \frac{\partial \widehat{XH}}{\partial \mathfrak{D}_j} \widehat{\mathfrak{D}}_i. \quad (12.167)$$

Because \widehat{XH} is constant and not dependent on the Euler angles its derivative is zero. Therefore

$$\frac{\partial \delta_i}{\partial \mathfrak{D}_j} = \widehat{XH} \frac{\partial \widehat{\mathfrak{D}}_i}{\partial \mathfrak{D}_j}. \quad (12.168)$$

The \mathfrak{D}_x gradient

The partial derivatives of the unit vector $\widehat{\mathfrak{D}}_x$ with respect to the Euler angles are

$$\frac{\partial \widehat{\mathfrak{D}}_x}{\partial \alpha} = \begin{pmatrix} -\cos \alpha \sin \gamma - \sin \alpha \cos \beta \cos \gamma \\ -\cos \alpha \cos \gamma + \sin \alpha \cos \beta \sin \gamma \\ -\sin \alpha \sin \beta \end{pmatrix}, \quad (12.169a)$$

$$\frac{\partial \widehat{\mathfrak{D}}_x}{\partial \beta} = \begin{pmatrix} -\cos \alpha \sin \beta \cos \gamma \\ \cos \alpha \sin \beta \sin \gamma \\ \cos \alpha \cos \beta \end{pmatrix}, \quad (12.169b)$$

$$\frac{\partial \widehat{\mathfrak{D}}_x}{\partial \gamma} = \begin{pmatrix} -\sin \alpha \cos \gamma - \cos \alpha \cos \beta \sin \gamma \\ \sin \alpha \sin \gamma - \cos \alpha \cos \beta \cos \gamma \\ 0 \end{pmatrix}. \quad (12.169c)$$

The \mathfrak{D}_y gradient

The partial derivatives of the unit vector $\widehat{\mathfrak{D}}_y$ with respect to the Euler angles are

$$\frac{\partial \widehat{\mathfrak{D}}_y}{\partial \alpha} = \begin{pmatrix} -\sin \alpha \sin \gamma + \cos \alpha \cos \beta \cos \gamma \\ -\sin \alpha \cos \gamma - \cos \alpha \cos \beta \sin \gamma \\ \cos \alpha \sin \beta \end{pmatrix}, \quad (12.170a)$$

$$\frac{\partial \widehat{\mathfrak{D}}_y}{\partial \beta} = \begin{pmatrix} -\sin \alpha \sin \beta \cos \gamma \\ \sin \alpha \sin \beta \sin \gamma \\ \sin \alpha \cos \beta \end{pmatrix}, \quad (12.170b)$$

$$\frac{\partial \widehat{\mathfrak{D}}_y}{\partial \gamma} = \begin{pmatrix} \cos \alpha \cos \gamma - \sin \alpha \cos \beta \sin \gamma \\ -\cos \alpha \sin \gamma - \sin \alpha \cos \beta \cos \gamma \\ 0 \end{pmatrix}. \quad (12.170c)$$

The \mathfrak{D}_z gradient

The partial derivatives of the unit vector $\widehat{\mathfrak{D}}_z$ with respect to the Euler angles are

$$\frac{\partial \widehat{\mathfrak{D}}_z}{\partial \alpha} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.171a)$$

$$\frac{\partial \widehat{\mathfrak{D}}_z}{\partial \beta} = \begin{pmatrix} -\cos \beta \cos \gamma \\ \cos \beta \sin \gamma \\ -\sin \beta \end{pmatrix}, \quad (12.171b)$$

$$\frac{\partial \widehat{\mathfrak{D}}_z}{\partial \gamma} = \begin{pmatrix} \sin \beta \sin \gamma \\ \sin \beta \cos \gamma \\ 0 \end{pmatrix}. \quad (12.171c)$$

12.12.3 The dot product Hessian of the ellipsoid

The second partial derivative of the dot product δ_i with respect to the orientational parameters \mathfrak{O}_j and \mathfrak{O}_k is

$$\frac{\partial^2 \delta_i}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} = \frac{\partial^2}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k} (\widehat{XH} \cdot \widehat{\mathfrak{D}}_i) = \widehat{XH} \frac{\partial^2 \widehat{\mathfrak{D}}_i}{\partial \mathfrak{O}_j \cdot \partial \mathfrak{O}_k}. \quad (12.172)$$

The \mathfrak{D}_x Hessian

The second partial derivatives of the unit vector $\widehat{\mathfrak{D}}_x$ with respect to the Euler angles are

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \alpha^2} = \begin{pmatrix} \sin \alpha \sin \gamma - \cos \alpha \cos \beta \cos \gamma \\ \sin \alpha \cos \gamma + \cos \alpha \cos \beta \sin \gamma \\ -\cos \alpha \sin \beta \end{pmatrix}, \quad (12.173a)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \alpha \cdot \partial \beta} = \begin{pmatrix} \sin \alpha \sin \beta \cos \gamma \\ -\sin \alpha \sin \beta \sin \gamma \\ -\sin \alpha \cos \beta \end{pmatrix}, \quad (12.173b)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \alpha \cdot \partial \gamma} = \begin{pmatrix} -\cos \alpha \cos \gamma + \sin \alpha \cos \beta \sin \gamma \\ \cos \alpha \sin \gamma + \sin \alpha \cos \beta \cos \gamma \\ 0 \end{pmatrix}, \quad (12.173c)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \beta^2} = \begin{pmatrix} -\cos \alpha \cos \beta \cos \gamma \\ \cos \alpha \cos \beta \sin \gamma \\ -\cos \alpha \sin \beta \end{pmatrix}, \quad (12.173d)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \beta \cdot \partial \gamma} = \begin{pmatrix} \cos \alpha \sin \beta \sin \gamma \\ \cos \alpha \sin \beta \cos \gamma \\ 0 \end{pmatrix}, \quad (12.173e)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_x}{\partial \gamma^2} = \begin{pmatrix} \sin \alpha \sin \gamma - \cos \alpha \cos \beta \cos \gamma \\ \sin \alpha \cos \gamma + \cos \alpha \cos \beta \sin \gamma \\ 0 \end{pmatrix}. \quad (12.173f)$$

The \mathfrak{D}_y Hessian

The second partial derivatives of the unit vector $\widehat{\mathfrak{D}}_y$ with respect to the Euler angles are

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \alpha^2} = \begin{pmatrix} -\cos \alpha \sin \gamma - \sin \alpha \cos \beta \cos \gamma \\ -\cos \alpha \cos \gamma + \sin \alpha \cos \beta \sin \gamma \\ -\sin \alpha \sin \beta \end{pmatrix}, \quad (12.174a)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \alpha \cdot \partial \beta} = \begin{pmatrix} -\cos \alpha \sin \beta \cos \gamma \\ \cos \alpha \sin \beta \sin \gamma \\ \cos \alpha \cos \beta \end{pmatrix}, \quad (12.174b)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \alpha \cdot \partial \gamma} = \begin{pmatrix} -\sin \alpha \cos \gamma - \cos \alpha \cos \beta \sin \gamma \\ \sin \alpha \sin \gamma - \cos \alpha \cos \beta \cos \gamma \\ 0 \end{pmatrix}, \quad (12.174c)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \beta^2} = \begin{pmatrix} -\sin \alpha \cos \beta \cos \gamma \\ \sin \alpha \cos \beta \sin \gamma \\ -\sin \alpha \sin \beta \end{pmatrix}, \quad (12.174d)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \beta \cdot \partial \gamma} = \begin{pmatrix} \sin \alpha \sin \beta \sin \gamma \\ \sin \alpha \sin \beta \cos \gamma \\ 0 \end{pmatrix}, \quad (12.174e)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_y}{\partial \gamma^2} = \begin{pmatrix} -\cos \alpha \sin \gamma - \sin \alpha \cos \beta \cos \gamma \\ -\cos \alpha \cos \gamma + \sin \alpha \cos \beta \sin \gamma \\ 0 \end{pmatrix}. \quad (12.174f)$$

The \mathfrak{D}_z Hessian

The second partial derivatives of the unit vector $\widehat{\mathfrak{D}}_z$ with respect to the Euler angles are

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \alpha^2} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.175a)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \alpha \cdot \partial \beta} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.175b)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \alpha \cdot \partial \gamma} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad (12.175c)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \beta^2} = \begin{pmatrix} \sin \beta \cos \gamma \\ -\sin \beta \sin \gamma \\ -\cos \beta \end{pmatrix}, \quad (12.175d)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \beta \cdot \partial \gamma} = \begin{pmatrix} \cos \beta \sin \gamma \\ \cos \beta \cos \gamma \\ 0 \end{pmatrix}, \quad (12.175e)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_z}{\partial \gamma^2} = \begin{pmatrix} \sin \beta \cos \gamma \\ -\sin \beta \sin \gamma \\ 0 \end{pmatrix}. \quad (12.175f)$$

12.13 Spheroidal dot product derivatives

12.13.1 The dot product of the spheroid

The single dot product of the spheroid is defined as

$$\delta_z = \widehat{XH} \cdot \widehat{\mathfrak{D}}_{\parallel}, \quad (12.176)$$

where \widehat{XH} is a unit vector parallel to the XH vector. $\widehat{\mathfrak{D}}_{\parallel}$ is a unit vector parallel to the unique axis of the diffusion tensor and can be expressed using the spherical angles where θ is the polar angle and ϕ is the azimuthal angle as

$$\widehat{\mathfrak{D}}_{\parallel} = \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix}. \quad (12.177)$$

12.13.2 The dot product gradient of the spheroid

The partial derivative of the dot product with respect to the orientational parameter \mathfrak{O}_i is

$$\frac{\partial \delta_z}{\partial \mathfrak{O}_i} = \frac{\partial}{\partial \mathfrak{O}_i} (\widehat{XH} \cdot \widehat{\mathfrak{D}}_{\parallel}) = \widehat{XH} \frac{\partial \widehat{\mathfrak{D}}_{\parallel}}{\partial \mathfrak{O}_i} + \frac{\partial \widehat{XH}}{\partial \mathfrak{O}_i} \widehat{\mathfrak{D}}_{\parallel}. \quad (12.178)$$

Because the XH bond vector is constant and not dependent on the spherical angles its derivative is zero. Therefore

$$\frac{\partial \delta_z}{\partial \mathfrak{O}_i} = \widehat{XH} \frac{\partial \widehat{\mathfrak{D}}_{\parallel}}{\partial \mathfrak{O}_i}. \quad (12.179)$$

The \mathfrak{D}_{\parallel} gradient

The partial derivatives of the unit vector $\widehat{\mathfrak{D}}_{\parallel}$ with respect to the spherical angles are

$$\frac{\partial \widehat{\mathfrak{D}}_{\parallel}}{\partial \theta} = \begin{pmatrix} \cos \theta \cos \phi \\ \cos \theta \sin \phi \\ -\sin \theta \end{pmatrix}, \quad (12.180a)$$

$$\frac{\partial \widehat{\mathfrak{D}}_{\parallel}}{\partial \phi} = \begin{pmatrix} -\sin \theta \sin \phi \\ \sin \theta \cos \phi \\ 0 \end{pmatrix}. \quad (12.180b)$$

12.13.3 The dot product Hessian of the spheroid

The second partial derivative of the single spheroidal dot product δ_z with respect to the orientational parameters \mathfrak{O}_i and \mathfrak{O}_j is

$$\frac{\partial^2 \delta_z}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} = \frac{\partial^2}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j} (\widehat{XH} \cdot \widehat{\mathfrak{D}}_{\parallel}) = \widehat{XH} \frac{\partial^2 \widehat{\mathfrak{D}}_{\parallel}}{\partial \mathfrak{O}_i \cdot \partial \mathfrak{O}_j}. \quad (12.181)$$

The \mathfrak{D}_{\parallel} Hessian

The second partial derivatives of the unit vector $\widehat{\mathfrak{D}}_{\parallel}$ with respect to the spherical angles are

$$\frac{\partial^2 \widehat{\mathfrak{D}}_{\parallel}}{\partial \theta^2} = \begin{pmatrix} -\sin \theta \cos \phi \\ -\sin \theta \sin \phi \\ -\cos \theta \end{pmatrix}, \quad (12.182a)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_{\parallel}}{\partial \theta \cdot \partial \phi} = \begin{pmatrix} -\cos \theta \sin \phi \\ \cos \theta \cos \phi \\ 0 \end{pmatrix}, \quad (12.182b)$$

$$\frac{\partial^2 \widehat{\mathfrak{D}}_{\parallel}}{\partial \phi^2} = \begin{pmatrix} -\sin \theta \cos \phi \\ -\sin \theta \sin \phi \\ 0 \end{pmatrix}. \quad (12.182c)$$

Part V

Reference

Chapter 13

Alphabetical listing of user functions

The following is a listing with descriptions of all the user functions available within the relax prompt and scripting environments. These are simply an alphabetical list of the docstrings which can normally be viewed in prompt mode by typing `help(function)`.

13.1 A warning about the formatting

The following documentation of the user functions has been automatically generated by a script which extracts and formats the docstring associated with each function. There may therefore be instances where the formatting has failed or where there are inconsistencies.

13.2 The list of functions

Each user function is presented within it's own subsection with the documentation broken into multiple parts: the synopsis, the default arguments, and the sections from the function's docstring.

13.2.1 The synopsis

The synopsis presents a brief description of the function. It is taken as the first line of the docstring when browsing the help system.

13.2.2 Defaults

This section lists all the arguments taken by the function and their default values. To invoke the function type the function name then in brackets type a comma separated list of arguments.

The first argument printed is always ‘self’ but you can safely ignore it. ‘self’ is part of the object oriented programming within Python and is automatically prefixed to the list of arguments you supply. Therefore you can’t provide ‘self’ as the first argument even if you do try.

13.2.3 Docstring sectioning

All other sections are created from the sectioning of the user function docstring.

```
relax> align_tensor.copy(tensor_from='Otting',
                           pipe_to='new')
```

13.2.4 align_tensor.copy



Synopsis

Copy alignment tensor data.

To copy the alignment tensor data of ‘Otting’ to that of ‘Otting new’, type one of:

```
relax> align_tensor.copy('Otting', tensor_to='Otting new')
```

```
relax> align_tensor.copy(tensor_from='Pf1',
                           tensor_to='Otting new')
```

Defaults

```
align_tensor.copy(tensor_from=None, pipe_from=None,
                  tensor_to=None, pipe_to=None)
```

Keyword arguments

tensor_from: The identification string of the alignment tensor to copy the data from.

pipe_from: The name of the data pipe to copy the alignment tensor data from.

tensor_to: The identification string of the alignment tensor to copy the data to.

pipe_to: The name of the data pipe to copy the alignment tensor data to.

Description

This will copy the alignment tensor data to a new tensor or a new data pipe. The destination data pipe must not contain any alignment tensor data corresponding to the tensor_to label. If the source or destination data pipes are not supplied, then both will default to the current data pipe. Both the source and destination tensor IDs must be supplied.

Prompt examples

To copy the alignment tensor data corresponding to ‘Pf1’ from the data pipe ‘old’ to the current data pipe, type one of:

```
relax> align_tensor.copy('Pf1', 'old')
```

```
relax> align_tensor.copy(tensor_from='Pf1',
                           pipe_from='old')
```

To copy the alignment tensor data corresponding to ‘Otting’ from the current data pipe to the data pipe new, type one of:

```
relax> align_tensor.copy('Otting', pipe_to='new')
```

13.2.5 align_tensor.delete**Synopsis**

Delete alignment tensor data from the relax data store.

Defaults

`align_tensor.delete(tensor=None)`

Keyword arguments

`tensor`: The alignment tensor identification string.

Description

This will delete the specified alignment tensor data from the current data pipe. If no tensor is specified, all tensors will be deleted.

13.2.6 align_tensor.display**Synopsis**

Display the alignment tensor information in full detail.

Defaults

`align_tensor.display(tensor=None)`

Keyword arguments

`tensor`: The alignment tensor identification string.

Description

This will show all information relating to the alignment tensor, including the different tensor forms:

Probability tensor.

Saupe order matrix.

Alignment tensor.

Magnetic susceptibility tensor.

All possible tensor parameters and information will also be shown (Eigensystem, GDO, Aa, Ar, \Re , eta, chi_ax, chi_rh, etc). The printout will be extensive.

If no tensor is specified, all tensors will be displayed.

13.2.7 align_tensor.fix



Synopsis

Fix all alignment tensors so that they do not change during optimisation.

Defaults

```
align_tensor.fix(id=None, fixed=True)
```

Keyword arguments

id: The alignment tensor identification string.

fixed: The flag specifying if the tensors should be fixed or variable.

Description

If the ID string is left unset, then all alignment tensors will be fixed.

13.2.8 align_tensor.init



Synopsis

Initialise an alignment tensor.

Defaults

```
align_tensor.init(tensor=None, align_id=None, domain=None, params=None, scale=1.0, angle_units='deg', param_types=2, errors=False)
```

Keyword arguments

tensor: The optional alignment tensor ID string, required if multiple tensors exist per alignment.

align_id: The alignment ID string that the tensor corresponds to.

domain: The optional domain ID string that the tensor corresponds to.

params: The alignment tensor data.

scale: The alignment tensor eigenvalue scaling value.

angle_units: The units for the angle parameters.

param_types: A flag to select different parameter combinations.

errors: A flag which determines if the alignment tensor data or its errors are being input.

Description

The tensor ID is only required if there are multiple unique tensors per alignment. An example is if internal domain motions cause multiple parts of the molecule to align differently. The tensor ID is optional and in the case of only a single tensor per alignment, the tensor can be identified using the alignment ID instead.

The alignment tensor parameters should be a tuple of floating point numbers (a list surrounded by round brackets). These correspond to the parameters of the tensor which can be specified by the parameter types whereby the values correspond to:

0 – {Sxx, Syy, Sxy, Sxz, Syz} (unitless),

1 – {Szz, Sxx-yy, Sxy, Sxz, Syz} (Pales default format),

2 – {Axx, Ayy, Axy, Axz, Ayz} (unitless),

-
- 3 – {Azz, Axx-yy, Axy, Axz, Ayz} (unitless),
 4 – {Axx, Ayy, Axy, Axz, Ayz} (units of Hertz),
 5 – {Azz, Axx-yy, Axy, Axz, Ayz} (units of Hertz),
 6 – {Pxx, Pyy, Pxy, Pxz, Pyz} (unitless),
 7 – {Pzz, Pxx-yy, Pxy, Pxz, Pyz} (unitless).

Other formats may be added later. The relationship between the Saupe order matrix S and the alignment tensor A is

$$S = 3/2 A.$$

The probability matrix P is related to the alignment tensor A by

$$A = P - 1/3 I,$$

where I is the identity matrix. For the alignment tensor to be supplied in Hertz, the bond vectors must all be of equal length.

Prompt examples

To set a rhombic tensor for the domain labelled ‘domain 1’ with the alignment named ‘super media’, type one of:

```
relax> align_tensor.init('domain 1', 'super
media', (-8.6322e-05, -5.5786e-04, -3
.1732e-05, 2.2927e-05, 2.8599e-04),
param_types=1)
```

```
relax> align_tensor.init(tensor='domain 1',
align_id='super media', params=(-8
.6322e-05, -5.5786e-04, -3.1732e-05, 2
.2927e-05, 2.8599e-04), param_types=1)
```

13.2.9 align_tensor.matrix_angles



Synopsis

Calculate the 5D angles between all alignment tensors.

Defaults

`align_tensor.matrix_angles(basis_set=0, tensors=None)`

Keyword arguments

`basis_set`: The basis set to operate with.

`tensors`: A list of the tensors to apply the calculation to. If None, all tensors are used.

Description

This will calculate the angles between all loaded alignment tensors for the current data pipe. The matrices are first converted to a 5D vector form and then the angles are calculated. The angles are dependent on the basis set. If the basis set is set to the default of 0, the vectors {Sxx, Syy, Sxy, Sxz, Syz} are used. If the basis set is set to 1, the vectors {Szz, Sxxy, Sxy, Sxz, Syz} are used instead.

13.2.10 align_tensor.reduction



Synopsis

Specify that one tensor is a reduction of another.

Defaults

```
align_tensor.reduction(full_tensor=None, red_tensor=None)
```

Keyword arguments

full_tensor: The full alignment tensor.

red_tensor: The reduced alignment tensor.

Description

Prior to optimisation of the N-state model and Frame Order theories using alignment tensors, which tensor is a reduction of which other tensor must be specified through this user function.

Prompt examples

To state that the alignment tensor loaded as ‘chi3 C-dom’ is a reduction of ‘chi3 N-dom’, type:

```
relax> align_tensor.reduction(full_tensor='chi3 N-dom', red_tensor='chi3 C-dom')
```

13.2.11 align_tensor.set_domain



Synopsis

Set the domain label for the alignment tensor.

Defaults

```
align_tensor.set_domain(tensor=None, domain=None)
```

Keyword arguments

tensor: The alignment tensor to assign the domain label to.

domain: The domain label.

Description

Prior to optimisation of the N-state model or Frame Order theories, the domain to which each alignment tensor belongs must be specified.

Prompt examples

To link the alignment tensor loaded as ‘chi3 C-dom’ to the C-terminal domain ‘C’, type:

```
relax> align_tensor.set_domain(tensor='chi3 C-dom', domain='C')
```

The relationships between the geometric and unitary basis sets are:

13.2.12 align_tensor.svd



$$\begin{aligned} S_{zz} &= -S_{xx} - S_{yy}, \\ S_{xxyy} &= S_{xx} - S_{yy}, \end{aligned}$$

Synopsis

Calculate the singular values and condition number for all alignment tensors.

The SVD values and condition number are dependent upon the basis set chosen.

Defaults

`align_tensor.svd(basis_set=0, tensors=None)`

Keyword arguments

`basis_set`: The basis set to operate with.

`tensors`: A list of the tensors to apply the calculation to. If None, all tensors are used.

Description

This will perform a singular value decomposition of all tensors loaded for the current data pipe. If the basis set is set to the default of 0, the matrix on which SVD will be performed is composed of the unitary basis set {Sxx, Syy, Sxy, Sxz, Syz} layed out as:

```
| Sxx1 Syy1 Sxy1 Sxz1 Syz1 |
| Sxx2 Syy2 Sxy2 Sxz2 Syz2 |
| Sxx3 Syy3 Sxy3 Sxz3 Syz3 |
| . . . . . |
| . . . . . |
| . . . . . |
| SxxN SyyN SxyN SxzN SyzN |
```

If `basis_set` is set to 1, the geometric basis set consisting of the stretching and skewing parameters Szz and Sxxyy respectively {Szz, Sxxyy, Sxy, Sxz, Syz} will be used instead. The matrix is:

```
| Szz1 Sxxyy1 Sxy1 Sxz1 Syz1 |
| Szz2 Sxxyy2 Sxy2 Sxz2 Syz2 |
| Szz3 Sxxyy3 Sxy3 Sxz3 Syz3 |
| . . . . . |
| . . . . . |
| . . . . . |
| SzzN SxxyyN SxyN SxzN SyzN |
```

13.2.13 angles.diff_frame



Synopsis

Calculate the angles defining the XH bond vector within the diffusion frame.

Defaults

`angles.diff_frame()`

Description

If the diffusion tensor is isotropic, then nothing will be done.

If the diffusion tensor is axially symmetric, then the angle α will be calculated for each XH bond vector.

If the diffusion tensor is asymmetric, then the three angles will be calculated.

13.2.14 bmrbcitation



Synopsis

Specify a citation to be added the BMRB data file.

Defaults

`bmrbcitation(cite_id=None, authors=None, doi=None, pubmed_id=None, full_citation=None, title=None, status='published', type='journal', journal_abbrev=None, journal_full=None, volume=None, issue=None, page_first=None, page_last=None, year=None)`

Keyword arguments

`cite_id`: The citation ID string.

`authors`: The list of authors. Each author element is a list of four elements (the first name, last name, first initial, and middle initials).

`doi`: The DOI number, e.g. ‘10.1000/182’.

`pubmed_id`: The identification code assigned to the publication by PubMed.

`full_citation`: The full citation as given in a reference list.

`title`: The title of the publication.

`status`: The status of the publication. This can be a value such as ‘published’, ‘submitted’, etc.

`type`: The type of publication, for example ‘journal’.

`journal_abbrev`: The standard journal abbreviation.

`journal_full`: The full journal name.

`volume`: The volume number.

`issue`: The issue number.

`page_first`: The first page number.

`page_last`: The last page number.

`year`: The publication year.

Description

The full_citation should be in a format similar to that used in a journal article by either cutting and pasting from another document or by typing. Please include author names, title, journal, page numbers, and year or equivalent information for the type of publication given.

The journal status can only be one of:

```
Set theory formulation of the model-
free problem and the diffusion seeded
model-free paradigm.", status="
published", type="journal",
journal_abbrev="Mol. Biosyst.",
journal_full="Molecular Biosystems",
volume=3, issue=7, page_first=483,
page_last=498, year=2007)
```

```
'preparation',
'in press',
'published',
'retracted',
'submitted'.
```

The citation type can only be one of:

```
'abstract',
'BMRB only',
'book',
'book chapter',
'internet',
'journal',
'personal communication',
'thesis'.
```

The standard journal abbreviation is that defined by the Chemical Abstract Services for the journal where the data are or will be published. If the data in the deposition are related to a J. Biomol. NMR paper, the value must be 'J. Biomol. NMR' to alert the BMRB annotators so that the deposition is properly processed. If the depositor truly does not know the journal, a value of 'not known' or 'na' is acceptable.

Prompt examples

To add the citation "d'Auvergne E. J., Gooley P. R. (2007). Set theory formulation of the model-free problem and the diffusion seeded model-free paradigm. Mol. Biosyst., 3(7), 483-494.", type:

```
relax> bmrbcitation(authors=[[ "Edward", "d"
Auvergne", "E.", "J."], [ "Paul", "
Gooley", "P.", "R."]], doi="10.1039/
b702202f", pubmed_id="17579774",
full_citation="d'Auvergne E. J., Gooley
P. R. (2007). Set theory formulation
of the model-free problem and the
diffusion seeded model-free paradigm.
Mol. Biosyst., 3(7), 483-494.", title="
```

13.2.15 bmrbl.display



Synopsis

Display the BMRB data in NMR-STAR format.

Defaults

```
bmrbl.display(version='3.1')
```

Keyword arguments

version: The version of the BMRB NMR-STAR format to display.

Description

This will print the BMRB NMR-STAR formatted data to STDOUT.

13.2.16 bmrbl.read



Synopsis

Read BMRB files in the NMR-STAR format.

Defaults

```
bmrbl.read(file=None, dir=None, version=None, sample_conditions=None)
```

Keyword arguments

file: The name of the BMRB NMR-STAR formatted file to read.

dir: The directory where the file is located.

version: The version of the BMRB NMR-STAR format to read. This is not necessary as the version is normally auto-detected.

sample_conditions: The sample conditions label in the NMR-STAR file to restrict loading to.

Description

This will allow most of the data from a BMRB NMR-STAR formatted file to be loaded into the relax data store. Note that an empty data pipe should be created for storing the data, and that currently only model-free data pipes can be used. Also, only one sample condition can be read per relax data pipe. Therefore if one of the sample conditions is not specified and multiple conditions exist in the NMR-STAR file, an error will be raised.

13.2.17 **bmrbscript**



Synopsis

Specify the scripts used in the analysis.

Defaults

```
bmrbscript(file=None, dir=None, analysis_type=None,
model_selection=None, engine='relax', model_elim=False,
universal_solution=False)
```

Keyword arguments

file: The name of the script file.

dir: The directory where the file is located.

analysis_type: The type of analysis performed.

model_selection: The model selection technique used, if relevant. For example ‘AIC’ model selection.

engine: The software engine used in the analysis.

model_elim: A model-free specific flag specifying if model elimination was performed.

universal_solution: A model-free specific flag specifying if the universal solution was sought after.

Description

This user function allows scripts used in the analysis to be included in the BMRB deposition. The following addition information may need to be specified with the script.

The analysis type must be set. Allowable values include all the data pipe types used in relax, ie:

‘frame_order’ – The Frame Order theories,

‘jw’ – Reduced spectral density mapping,

‘mf’ – Model-free analysis,

‘N-state’ – N-state model of domain motions,

‘noe’ – Steady state NOE calculation,

‘relax_fit’ – Relaxation curve fitting,

The model selection technique only needs to be set if the script selects between different mathematical models. This can be anything, but the following are recommended:

‘AIC’ – Akaike’s Information Criteria.

‘AICc’ – Small sample size corrected AIC.

‘BIC’ – Bayesian or Schwarz Information Criteria.

‘Bootstrap’ – Bootstrap model selection.

‘CV’ – Single-item-out cross-validation.

‘Expect’ – The expected overall discrepancy (the true values of the parameters are required).

‘Farrow’ – Old model-free method by Farrow et al., 1994.

‘Palmer’ – Old model-free method by Mandel et al., 1995.

‘Overall’ – The realised overall discrepancy (the true values of the parameters are required).

The engine is the software used in the calculation, optimisation, etc. This can be anything, but those recognised by relax (automatic program info, citations, etc. added) include:

‘relax’ – hence relax was used for the full analysis.

‘modelfree4’ – Art Palmer’s Modelfree4 program was used for optimising the model-free parameter values.

‘dasha’ – The Dasha program was used for optimising the model-free parameter values.

‘curvefit’ – Art Palmer’s curvefit program was used to determine the R₁ or R₂ values.

The model_elim flag is model-free specific and should be set if the methods from ”d’Auvergne, E. J. and Gooley, P. R. (2006). Model-free model elimination: A new step in the model-free dynamic analysis of NMR relaxation data. J. Biomol. NMR, 35(2), 117-135.” were used. This should be set to True for the full_analysis.py script.

The universal_solution flag is model-free specific and should be set if the methods from ”d’Auvergne E. J., Gooley P. R. (2007). Set theory formulation of the model-free problem and the diffusion seeded model-free paradigm. Mol. Biosyst., 3(7), 483-494.” were used. This should be set to True for the full_analysis.py script.

Prompt examples

For BMRB deposition, to specify that the full_analysis.py script was used, type one of:

```
relax> bmrbb.script('full_analysis.py', 
    model_free', 'AIC', 'relax', True, True
)

relax> bmrbb.script(file='full_analysis.py',
    dir=None, analysis_type='model-free',
    model_selection='AIC', engine='relax',
    model_elim=True, universal_solution=
    True)
```

13.2.18 bmrbb.software



Synopsis

Specify the software used in the analysis.

Defaults

```
bmrbb.software(name=None, version=None, url=None,
    vendor_name=None, cite_ids=None, tasks=None)
```

Keyword arguments

name: The name of the software program utilised.

version: The version of the software, if applicable.

url: The web address of the software.

vendor_name: The name of the company or person behind the program.

cite_ids: A list of the BMRB citation ID numbers.

tasks: A list of all the tasks performed by the software.

Description

This user function allows the software used in the analysis to be specified in full detail.

For the tasks list, this should be a python list of strings (eg. ['spectral processing']). Although not restricted to these, the values suggested by the BMRB are:

```
'chemical shift assignment',
'chemical shift calculation',
'collection',
'data analysis',
'geometry optimization',
'peak picking',
'processing',
'refinement',
'structure solution'
```

Prompt examples

For BMRB deposition, to say that Sparky was used in the analysis, type:

```
relax> cite_id = bmrb.citation(authors=[["Tom", "Goddard", "T.", "D."], ["D.", "Kneller", "D.", "G."]], title="Goddard, T. D. and Kneller, D. G., SPARKY 3, University of California, San Francisco.")

relax> bmrb.software("Sparky", version="3.110", url="http://www.cgl.ucsf.edu/home/sparky/", vendor_name="Goddard, T. D.", cite_ids=[cite_id], tasks=["spectral analysis"])
```

13.2.19 bmrb.software_select



Synopsis

Select the software used in the analysis.

Defaults

`bmrb.software_select(name=None, version=None)`

Keyword arguments

`name`: The name of the software program utilised.

`version`: The version of the software, if applicable.

Description

Rather than specifying all the information directly, this user function allows the software packaged used in the analysis to be selected by name. The programs currently supported are:

‘NMRPipe’ – <http://spin.niddk.nih.gov/NMRPipe/>

‘Sparky’ – <http://www.cgl.ucsf.edu/home/sparky/>

More can be added if all relevant information (program name, description, website, original citation, purpose, etc.) is emailed to relax-users@gna.org.

Note that relax is automatically added to the BMRB file.

Prompt examples

For BMRB deposition, to say that both NMRPipe and Sparky were used prior to relax, type:

```
relax> bmrb.software_select('NMRPipe')

relax> bmrb.software_select('Sparky',
    version='3.113')
```

13.2.20 bmrbl.thiol_state



Synopsis

Select the thiol state of the system.

Defaults

bmrbl.thiol_state(state=None)

Keyword arguments

state: The thiol state.

Description

The thiol state can be any text, thought the BMRB suggests the following:

```
'all disulfide bound',
'all free',
'all other bound',
'disulfide and other bound',
'free and disulfide bound',
'free and other bound',
'free disulfide and other bound',
'not available',
'not present',
'not reported',
'unknown'.
```

Alternatively the pure states ‘reduced’ or ‘oxidised’ could be specified.

Prompt examples

For BMRB deposition, to say that the protein studied is in the oxidised state, ttype one of:

```
relax> bmrbl.thiol_state('oxidised')
```

```
relax> bmrbl.thiol_state(state='oxidised')
```

13.2.21 bmrbl.write



Synopsis

Write the results to a BMRB NMR-STAR formatted file.

Defaults

bmrbl.write(file=None, dir='pipe_name', version='3.1', force=False)

Keyword arguments

file: The name of the BMRB file to output results to. Optionally this can be a file object, or any object with a write() method.

dir: The directory name.

version: The NMR-STAR dictionary format version to create.

force: A flag which if True will cause the any pre-existing file to be overwritten.

Description

This will create a NMR-STAR formatted file of the data in the current data pipe for BMRB deposition.

In the prompt/script UI modes, to place the BMRB file in the current working directory, set dir to None. If dir is set to the special name ‘pipe_name’, then the results file will be placed into a directory with the same name as the current data pipe.

13.2.22 bruker.read**Synopsis**

Read a Bruker Dynamics Center (DC) relaxation data file.

Defaults

```
bruker.read(ri_id=None, file=None, dir=None)
```

Keyword arguments

ri_id: The relaxation data ID string. This must be a unique identifier.

file: The name of the Bruker Dynamics Center file containing the relaxation data.

dir: The directory where the file is located.

Description

This user function is used to load all of the data out of a Bruker Dynamics Center (DC) relaxation data file for subsequent analysis within relax. Currently the R₁ and R₂ relaxation rates and steady-state NOE data is supported.

13.2.23 calc**Synopsis**

Calculate the function value.

Defaults

```
calc(verbosity=1)
```

Keyword arguments

verbosity: The amount of information to print to screen. Zero corresponds to minimal output while higher values increase the amount of output. The default value is 1.

Description

This will call the target function for the analysis type associated with the current data pipe using the current parameter values. This can be used to find, for example, the chi-squared value for different parameter values.

13.2.24 chemical_shift.read

 ω 

Synopsis

Read chemical shifts from a file.

Defaults

```
chemical_shift.read(file=None, dir=None, spin_id_col=
None, mol_name_col=None, res_num_col=None,
res_name_col=None, spin_num_col=None, spin_name_col=
None, sep=None, spin_id=None)
```

Keyword arguments

file: The name of the peak list of generic formatted file containing the chemical shifts.

dir: The directory where the file is located.

spin_id_col: The spin ID string column used by the generic file format (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column used by the generic file format (alternative to the spin ID column).

res_num_col: The residue number column used by the generic file format (alternative to the spin ID column).

spin_num_col: The spin number column used by the generic file format (alternative to the spin ID column).

spin_name_col: The spin name column used by the generic file format (alternative to the spin ID column).

sep: The column separator used by the generic format (the default is white space).

spin_id: The spin ID string used to restrict the loading of data to certain spin subsets.

Description

This will read chemical shifts from a peak list or a generic column formatted file.

Prompt examples

The following commands will read the chemical shifts out of the Sparky peak list ‘10ms.list’:

```
relax> chemical_shift.read('10ms.list')
```

13.2.25 consistency_tests.set_frq

 ω

Synopsis

Select which relaxation data to use in the consistency tests by NMR spectrometer frequency.

Defaults

```
consistency_tests.set_frq(frq=None)
```

Keyword arguments

frq: The spectrometer frequency in Hz. This must match the currently loaded data to the last decimal point. See the ‘sfrq’ parameter in the Varian procpar file or the ‘SF01’ parameter in the Bruker acqus file.

Description

This will select the relaxation data to use in the consistency tests corresponding to the given frequencies. The data is selected by the spectrometer frequency in Hertz, which should be set to the exact value (see the ‘sfrq’ parameter in the Varian procpar file or the ‘SF01’ parameter in the Bruker acqus file). Note thought that the R₁, R₂ and NOE are all expected to have the exact same frequency in the J(ω) mapping analysis (to the last decimal point).

Prompt examples

```
relax> consistency_tests.set_frq(600.0 * 1e6
)
```

```
relax> consistency_tests.set_frq(frq=600.0 *
1e6)
```

13.2.26 dasha.create



Synopsis

Create the Dasha script.

Defaults

```
dasha.create(algor='LM', dir=None, force=False)
```

Keyword arguments

algor: The minimisation algorithm.

dir: The directory to place the files.

force: A flag which if set to True will cause the results file to be overwritten if it already exists.

Description

The script file created is called ‘`dir/dasha_script`’.

Optimisation algorithms

The two minimisation algorithms within Dasha are accessible through the algorithm which can be set to:

‘LM’ – The Levenberg-Marquardt algorithm,

‘NR’ – Newton-Raphson algorithm.

For Levenberg-Marquardt minimisation, the function ‘`lmin`’ will be called, while for Newton-Raphson, the function ‘`min`’ will be executed.

13.2.27 dasha.execute



Synopsis

Perform a model-free optimisation using Dasha.

Defaults

```
dasha.execute(dir=None, force=False, binary='dasha')
```

Keyword arguments

dir: The directory to place the files.

force: A flag which if set to True will cause the results file to be overwritten if it already exists.

binary: The name of the executable Dasha program file.

Description

Dasha will be executed as

```
$ dasha < dasha_script | tee dasha_results
```

If you would like to use a different Dasha executable file, change the binary name to the appropriate file name. If the file is not located within the environment’s path, include the full path in front of the binary file name.

13.2.28 dasha.extract**Synopsis**

Extract data from the Dasha results file.

Defaults

`dasha.extract(dir=None)`

Keyword arguments

`dir:` The directory where the file ‘`dasha_results`’ is found.

Description

The model-free results will be extracted from the Dasha results file ‘`dasha_results`’ located in the given directory.

13.2.29 deselect.all**Synopsis**

Deselect all spins in the current data pipe.

Defaults

`deselect.all()`

Description

This will deselect all spins, irregardless of their current state.

Prompt examples

To deselect all spins, simply type:

`relax> deselect.all()`

Prompt examples

13.2.30 deselect.interatom



Synopsis

Deselect specific interatomic data containers.

Defaults

```
deselect.interatom(spin_id1=None, spin_id2=None,
boolean='AND', change_all=False)
```

Keyword arguments

spin_id1: The spin ID string of the first spin of the interatomic data container.

spin_id2: The spin ID string of the second spin of the interatomic data container.

boolean: The boolean operator specifying how interatomic data containers should be selected.

change_all: A flag specifying if all other interatomic data containers should be changed.

Description

This is used to deselect specific interatomic data containers which store information about spin pairs such as RDCs, NOEs, dipole-dipole pairs involved in relaxation, etc. The ‘`change_all`’ flag default is False meaning that all interatomic data containers currently either selected or deselected will remain that way. Setting this to True will cause all interatomic data containers not specified by the spin ID strings to be deselected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

To deselect all N-H backbone bond vectors of a protein, assuming these interatomic data containers have been already set up, type one of:

```
relax> deselect.interatom('ON', 'OH')
```

```
relax> deselect.interatom(spin_id1='ON',
                           spin_id2='OH')
```

To deselect all H-H interatomic vectors of a small organic molecule, type one of:

```
relax> deselect.interatom('OH*', 'OH*')
```

```
relax> deselect.interatom(spin_id1='OH*',
                           spin_id2='OH*')
```

Table 13.1: Boolean operators and their effects on selections

Spin system or interatomic data container	1	2	3	4	5	6	7	8	9
Original selection	0	1	1	1	1	0	1	0	1
New selection	0	1	1	1	1	1	0	0	0
OR	0	1	1	1	1	1	1	0	1
NOR	1	0	0	0	0	0	0	1	0
AND	0	1	1	1	1	0	0	0	0
NAND	1	0	0	0	0	1	1	1	1
XOR	0	0	0	0	0	1	1	0	1
XNOR	1	1	1	1	1	0	0	1	0

13.2.31 deselect.read



Synopsis

Deselect the spins contained in a file.

Defaults

```
deselect.read(file=None, dir=None, spin_id_col=None,
mol_name_col=None, res_num_col=None, res_name_col=
None, spin_num_col=None, spin_name_col=None, sep=
None, spin_id=None, boolean='AND', change_all=False)
```

Keyword arguments

file: The name of the file containing the list of spins to deselect.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

sep: The column separator (the default is white space).



spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

boolean: The boolean operator specifying how spins should be selected.

change_all: A flag specifying if all other spins should be changed.

Description

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number, residue name, spin number and/or spin name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID string can be used to restrict the reading to certain spin types, for example only 15N spins when only residue information is in the file.

Empty lines and lines beginning with a hash are ignored.

The ‘change all’ flag default is False meaning that all spins currently either selected or deselected will remain that way. Setting this to True will cause all spins not specified in the file to be selected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

Prompt examples

To deselect all overlapped residues listed with residue numbers in the first column of the file ‘unresolved’, type one of:

```
relax> deselect.read('unresolved',
    res_num_col=1)

relax> deselect.read(file='unresolved',
    res_num_col=1)

To deselect the spins in the second column of the relax-
ation data file 'r1.600' while selecting all other spins, for
example type:

relax> deselect.read('r1.600', spin_num_col
    =2, change_all=True)

relax> deselect.read(file='r1.600',
    spin_num_col=2, change_all=True)
```

13.2.32 deselect.reverse



Synopsis

Reversal of the spin selection for the given spins.

Defaults

```
deselect.reverse(spin_id=None)
```

Keyword arguments

`spin_id`: The spin ID string.

Description

By supplying the spin ID string, a subset of spins can have their selection status reversed.

Description

To deselect all currently selected spins and select those which are deselected type:

```
relax> deselect.reverse()
```

13.2.33 deselect.spin



Synopsis

Deselect specific spins.

Defaults

```
deselect.spin(spin_id=None, boolean='AND', change_all=False)
```

Keyword arguments

spin_id: The spin ID string.

boolean: The boolean operator specifying how spins should be deselected.

change_all: A flag specifying if all other spins should be changed.

Description

The ‘change all’ flag default is False meaning that all spins currently either selected or deselected will remain that way. Setting this to True will cause all spins not specified by the spin ID string to be deselected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

Prompt examples

To deselect all glycines and alanines, type:

```
relax> deselect.spin(spin_id=':GLY|:ALA')
```

To deselect residue 12 MET type:

```
relax> deselect.spin(':12')
```

```
relax> deselect.spin(spin_id=':12')
```

```
relax> deselect.spin(spin_id=':12&:MET')
```

13.2.34 diffusion_tensor.copy



Synopsis

Copy diffusion tensor data from one data pipe to another.

Defaults

```
diffusion_tensor.copy(pipe_from=None, pipe_to=None)
```

Keyword arguments

pipe_from: The name of the data pipe to copy the diffusion tensor data from.

pipe_to: The name of the data pipe to copy the diffusion tensor data to.

Description

This will copy the diffusion tensor data between data pipes. The destination data pipe must not contain any diffusion tensor data. If the source or destination data pipes are not supplied, then both will default to the current data pipe (hence specifying at least one is essential).

Prompt examples

To copy the diffusion tensor from the data pipe ‘m1’ to the current data pipe, type:

```
relax> diffusion_tensor.copy('m1')
```

```
relax> diffusion_tensor.copy(pipe_from='m1')
```

To copy the diffusion tensor from the current data pipe to the data pipe ‘m9’, type:

```
relax> diffusion_tensor.copy(pipe_to='m9')
```

To copy the diffusion tensor from the data pipe ‘m1’ to ‘m2’, type:

```
relax> diffusion_tensor.copy('m1', 'm2')
```

```
relax> diffusion_tensor.copy(pipe_from='m1',
    pipe_to='m2')
```

13.2.35 diffusion_tensor.delete**Synopsis**

Delete the diffusion tensor data from the relax data store.

Defaults

diffusion_tensor.delete()

Description

This will delete all diffusion tensor data from the current data pipe.

13.2.36 diffusion_tensor.display**Synopsis**

Display the diffusion tensor information.

Defaults

diffusion_tensor.display()

Description

This will display all of the diffusion tensor information of the current data pipe.

13.2.37 diffusion_tensor.init



Synopsis

Initialise the diffusion tensor.

Defaults

```
diffusion_tensor.init(params=None, time_scale=1.0,
d_scale=1.0, angle_units='deg', param_types=0,
spheroid_type=None, fixed=True)
```

Keyword arguments

params: The diffusion tensor data.

time_scale: The correlation time scaling value.

d_scale: The diffusion tensor eigenvalue scaling value.

angle_units: The units for the angle parameters.

param_types: A flag to select different parameter combinations.

spheroid_type: A string which, if supplied together with spheroid parameters, will restrict the tensor to either being ‘oblate’ or ‘prolate’.

fixed: A flag specifying whether the diffusion tensor is fixed or can be optimised.

The sphere (isotropic diffusion)

When the molecule diffuses as a sphere, all three eigenvalues of the diffusion tensor are equal, $\mathfrak{D}_x = \mathfrak{D}_y = \mathfrak{D}_z$. In this case, the orientation of the XH bond vector within the diffusion frame is inconsequential to relaxation, hence, the spherical or Euler angles are undefined. Therefore solely a single geometric parameter, either τ_m or \mathfrak{D}_{iso} , can fully and sufficiently parameterise the diffusion tensor. The correlation function for the global rotational diffusion is

$$C(\tau) = -\frac{1}{5} e^{-\tau / \tau_m},$$

To select isotropic diffusion, the parameter should be a single floating point number. The number is the value of the isotropic global correlation time, τ_m , in seconds. To specify the time in nanoseconds, set the time scale to 1e-9. Alternative parameters can be used by changing the ‘param_types’ flag to the following integers

0 – {tm} (Default),

1 – {Diso},

where

$$1 / \tau_m = 6\mathfrak{D}_{iso}.$$

The spheroid (axially symmetric diffusion)

When two of the three eigenvalues of the diffusion tensor are equal, the molecule diffuses as a spheroid. Four pieces of information are required to specify this tensor, the two geometric parameters, \mathfrak{D}_{iso} and \mathfrak{D}_a , and the two orientational parameters, the polar angle θ and the azimuthal angle ϕ describing the orientation of the axis of symmetry. The correlation function of the global diffusion is

$$C(\tau) = -\frac{1}{5} e^{-\tau / \tau_m},$$

$$\begin{aligned} & \quad \text{--} \frac{1}{5} \sum_{i=-1}^{+1} c_i \cos(i\phi) \cos(i\theta) e^{-\tau / \tau_m}, \\ & \quad \text{--} \frac{1}{5} \sum_{i=-1}^{+1} c_i \sin(i\phi) \cos(i\theta) e^{-\tau / \tau_m}, \end{aligned}$$

where

$$c_{-1} = 1/4 (3 \delta_z^2 - 1)^2,$$

$$c_0 = 3 \delta_z^2 (1 - \delta_z^2),$$

$$c_1 = 3/4 (\delta_z^2 - 1)^2,$$

and

$$1 / \tau_{-1} = 6\mathfrak{D}_{iso} - 2\mathfrak{D}_a,$$

$$1 / \tau_0 = 6\mathfrak{D}_{iso} - \mathfrak{D}_a,$$

$$1 / \tau_1 = 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a.$$

The direction cosine δ_z is defined as the cosine of the angle α between the XH bond vector and the unique axis of the diffusion tensor.

To select axially symmetric anisotropic diffusion, the parameters should be a tuple of floating point numbers of length four. A tuple is a type of data structure enclosed in round brackets, the elements of which are separated by commas. Alternative sets of parameters, ‘param_types’, are

0 – $\{\tau_m, \mathfrak{D}_a, \theta, \phi\}$ (Default),

1 – $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \theta, \phi\}$,

2 – $\{\tau_m, \mathfrak{D}_{ratio}, \theta, \phi\}$,

3 – $\{\mathfrak{D}_{||}, \mathfrak{D}_{\perp}, \theta, \phi\}$,

4 – $\{\mathfrak{D}_{iso}, \mathfrak{D}_{ratio}, \theta, \phi\}$,

```


$$\text{C}(\tau) = - \frac{1}{5} \sum_{i=-2}^{2} \text{ci}_i e^{-\frac{\tau}{\tau_i}}$$


```

where

$$\begin{aligned}\tau_m &= 1 / 6\mathfrak{D}_{iso}, \\ \mathfrak{D}_{iso} &= 1/3 (\mathfrak{D}_{||} + 2\mathfrak{D}_{\perp}), \\ \mathfrak{D}_a &= \mathfrak{D}_{||} - \mathfrak{D}_{\perp}, \\ \mathfrak{D}_{ratio} &= \mathfrak{D}_{||} / \mathfrak{D}_{\perp}.\end{aligned}$$

The spherical angles $\{\theta, \phi\}$ orienting the unique axis of the diffusion tensor within the PDB frame are defined between

$$0 \leq \theta \leq \pi,$$

$$0 \leq \phi \leq 2\pi,$$

while the angle α which is the angle between this axis and the given XH bond vector is defined between

$$0 \leq \alpha \leq 2\pi.$$

The spheroid type should be ‘oblate’, ‘prolate’, or None. This will be ignored if the diffusion tensor is not axially symmetric. If ‘oblate’ is given, then the constraint $\mathfrak{D}_a \leq 0$ is used while if ‘prolate’ is given, then the constraint $\mathfrak{D}_a \geq 0$ is used. If nothing is supplied, then \mathfrak{D}_a will be allowed to have any values. To prevent minimisation of diffusion tensor parameters in a space with two minima, it is recommended to specify which tensor is to be minimised, thereby partitioning the two minima into the two subspaces along the boundary $\mathfrak{D}_a = 0$.

The ellipsoid (rhombic diffusion)

When all three eigenvalues of the diffusion tensor are different, the molecule diffuses as an ellipsoid. This diffusion is also known as fully anisotropic, asymmetric, or rhombic. The full tensor is specified by six pieces of information, the three geometric parameters \mathfrak{D}_{iso} , \mathfrak{D}_a , and \mathfrak{D}_r representing the isotropic, anisotropic, and rhombic components of the tensor, and the three Euler angles α , β , and γ orienting the tensor within the PDB frame. The correlation function is

where the weights on the exponentials are

$$\begin{aligned}c_{-2} &= 1/4 (d + e), \\ c_{-1} &= 3 \delta_y^2 \delta_z^2, \\ c_0 &= 3 \delta_x^2 \delta_z^2, \\ c_1 &= 3 \delta_x^2 \delta_y^2, \\ c_2 &= 1/4 (d + e).\end{aligned}$$

Let

$$\mathfrak{R} = \sqrt{1 + 3\mathfrak{D}_r},$$

then

$$\begin{aligned}d &= 3 (\delta_x^4 + \delta_y^4 + \delta_z^4) - 1, \\ e &= -1 / \mathfrak{R} ((1 + 3\mathfrak{D}_r)(\delta_x^4 + 2\delta_y^2 \delta_z^2) + \\ &\quad (1 - 3\mathfrak{D}_r)(\delta_y^4 + 2\delta_x^2 \delta_z^2) - 2(\delta_z^4 + 2\delta_x^2 \delta_y^2)).\end{aligned}$$

The correlation times are

$$\begin{aligned}1 / \tau_{-2} &= 6\mathfrak{D}_{iso} - 2\mathfrak{D}_a \cdot \mathfrak{R}, \\ 1 / \tau_{-1} &= 6\mathfrak{D}_{iso} - \mathfrak{D}_a (1 + 3\mathfrak{D}_r), \\ 1 / \tau_0 &= 6\mathfrak{D}_{iso} - \mathfrak{D}_a (1 - 3\mathfrak{D}_r), \\ 1 / \tau_1 &= 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a, \\ 1 / \tau_2 &= 6\mathfrak{D}_{iso} + 2\mathfrak{D}_a \cdot \mathfrak{R}.\end{aligned}$$

The three direction cosines δ_x , δ_y , and δ_z are the coordinates of a unit vector parallel to the XH bond vector. Hence the unit vector is $[\delta_x, \delta_y, \delta_z]$.

To select fully anisotropic diffusion, the parameters should be a tuple of length six. A tuple is a type of data structure enclosed in round brackets, the elements of which are separated by commas. Alternative sets of parameters, ‘param_types’, are

0 – $\{\tau_m, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$ (Default),

1 – $\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$,

2 – $\{\mathfrak{D}_x, \mathfrak{D}_y, \mathfrak{D}_z, \alpha, \beta, \gamma\}$,

3 – {Dxx, Dyy, Dzz, Dxy, Dxz, Dyz},

where

$$\begin{aligned}\tau_m &= 1 / 6\mathfrak{D}_{iso}, \\ \mathfrak{D}_{iso} &= 1/3 (\mathfrak{D}_x + \mathfrak{D}_y + \mathfrak{D}_z), \\ \mathfrak{D}_a &= \mathfrak{D}_z - (\mathfrak{D}_x + \mathfrak{D}_y)/2, \\ \mathfrak{D}_r &= (\mathfrak{D}_y - \mathfrak{D}_x)/2\mathfrak{D}_a.\end{aligned}$$

The angles α , β , and γ are the Euler angles describing the diffusion tensor within the PDB frame. These angles are defined using the z-y-z axis rotation notation where α is the initial rotation angle around the z-axis, β is the rotation angle around the y-axis, and γ is the final rotation around the z-axis again. The angles are defined between

$$\begin{aligned}0 \leq \alpha \leq 2\pi, \\ 0 \leq \beta \leq \pi, \\ 0 \leq \gamma \leq 2\pi.\end{aligned}$$

Within the PDB frame, the XH bond vector is described using the spherical angles θ and ϕ where θ is the polar angle and ϕ is the azimuthal angle defined between

$$\begin{aligned}0 \leq \theta \leq \pi, \\ 0 \leq \phi \leq 2\pi.\end{aligned}$$

When param_types is set to 3, then the elements of the diffusion tensor matrix defined within the PDB frame can be supplied.

Units

The correlation time scaling value should be a floating point number. The only parameter affected by this value is τ_m .

The diffusion tensor eigenvalue scaling value should also be a floating point number. Parameters affected by this value are \mathfrak{D}_{iso} , $\mathfrak{D}_{||}$, \mathfrak{D}_{\perp} , \mathfrak{D}_a , \mathfrak{D}_x , \mathfrak{D}_y , and \mathfrak{D}_z . Significantly, \mathfrak{D}_r is not affected.

The units for the angle parameters should be either ‘deg’ or ‘rad’. Parameters affected are θ , ϕ , α , β , and γ .

Prompt examples

To set an isotropic diffusion tensor with a correlation time of 10 ns, type:

```
relax> diffusion_tensor.init(10e-9)

relax> diffusion_tensor.init(params=10e-9)

relax> diffusion_tensor.init(10.0, 1e-9)

relax> diffusion_tensor.init(params=10.0,
                             time_scale=1e-9, fixed=True)
```

To select axially symmetric diffusion with a τ_m value of 8.5 ns, \mathfrak{D}_{ratio} of 1.1, θ value of 20 degrees, and ϕ value of 20 degrees, type:

```
relax> diffusion_tensor.init((8.5e-9, 1.1,
                               20.0, 20.0), param_types=2)
```

To select a spheroid diffusion tensor with a $\mathfrak{D}_{||}$ value of 1.698e7, \mathfrak{D}_{\perp} value of 1.417e7, θ value of 67.174 degrees, and ϕ value of -83.718 degrees, type one of:

```
relax> diffusion_tensor.init((1.698e7, 1
                               .417e7, 67.174, -83.718), param_types
                               =3)
```

```
relax> diffusion_tensor.init(params=(1.698e7
                                      , 1.417e7, 67.174, -83.718),
                               param_types=3)
```

```
relax> diffusion_tensor.init((1.698e-1, 1
                               .417e-1, 67.174, -83.718), param_types
                               =3, d_scale=1e8)
```

```
relax> diffusion_tensor.init(params=(1.698e-1
                                      , 1.417e-1, 67.174, -83.718),
                               param_types=3, d_scale=1e8)
```

```
relax> diffusion_tensor.init((1.698e-1, 1
                               .417e-1, 1.1724, -1.4612), param_types
                               =3, d_scale=1e8, angle_units='rad')
```

```
relax> diffusion_tensor.init(params=(1.698e-1
                                      , 1.417e-1, 1.1724, -1.4612),
                               param_types=3, d_scale=1e8, angle_units
                               ='rad', fixed=True)
```

To select ellipsoidal diffusion, type:

```
relax> diffusion_tensor.init((1.340e7, 1
                               .516e7, 1.691e7, -82.027, -80.573, 65
                               .568), param_types=2)
```

13.2.38 domain**Synopsis**

Definition of structural domains.

Defaults

domain(id=None, spin_id=None)

Keyword arguments

id: The ID string used to identify molecular domains.

spin_id: The spin ID string of all atomic members of the domain.

Description

This is used to define structural domains. Multiple domains can be defined, and these can overlap. Rather than labelling the currently loaded spins with the ID string, the spin ID string is stored for later use. This allows new spins to be loaded later and still be included within the same domain.

13.2.39 dx.execute**Synopsis**

Execute an OpenDX program.

Defaults

dx.execute(file_prefix='map', dir='dx', dx_exe='dx', vp_exec=True)

Keyword arguments

file_prefix: The file name prefix. For example if file is set to ‘temp’, then the OpenDX program temp.net will be loaded.

dir: The directory to change to for running OpenDX. If this is set to None, OpenDX will be run in the current directory.

dx_exe: The OpenDX executable file.

vp_exec: A flag specifying whether to execute the visual program automatically at start-up. The default of True causes the program to be executed.

Description

This will execute OpenDX to display the space maps created previously by the δ_x .map user function. This will work for any type of OpenDX map.

13.2.40 dx.map



Synopsis

Create a map of the given space in OpenDX format.

Defaults

```
dx.map(params=None, map_type='Iso3D', spin_id=None,
inc=20, lower=None, upper=None, axis_incs=5,
file_prefix='map', dir='dx', point=None, point_file=
'point', remap=None)
```

Keyword arguments

params: The parameters to be mapped. This should be an array of strings, the meanings of which are described below.

map_type: The type of map to create. For example the default, a 3D isosurface, the type is ‘Iso3D’. See below for more details.

spin_id: The spin ID string.

inc: The number of increments to map in each dimension. This value controls the resolution of the map.

lower: The lower bounds of the space. If you wish to change the lower bounds of the map then supply an array of length equal to the number of parameters in the model. A lower bound for each parameter must be supplied. If nothing is supplied then the defaults will be used.

upper: The upper bounds of the space. If you wish to change the upper bounds of the map then supply an array of length equal to the number of parameters in the model. A upper bound for each parameter must be supplied. If nothing is supplied then the defaults will be used.

axis_incs: The number of increments or ticks displaying parameter values along the axes of the OpenDX plot.

file_prefix: The file name. All the output files are prefixed with this name. The main file containing the data points will be called the value of ‘file’. The OpenDX program will be called ‘file.net’ and the OpenDX import file will be called ‘file.general’.

dir: The directory to output files to. Set this to ‘None’ if you do not want the files to be placed in subdirectory. If the directory does not exist, it will be created.

point: An array of parameter values where a point in the map, shown as a red sphere, will be placed. The length must be equal to the number of parameters.

point_file: The name of that the point output files will be prefixed with.

remap: A user supplied remapping function. This function will receive the parameter array and must return an array of equal length.

Description

This will map the space corresponding to the spin identifier and create the OpenDX files. The map type can be changed to one of the following supported map types:

Please see Table 13.2 on page 262.

Regular expression

The python function ‘match’, which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

‘[]’ – A sequence or set of characters to match to a single character. For example, ‘[sS]2’ will match both ‘S2’ and ‘s2’.

‘^’ – Match the start of the string.

‘\$’ – Match the end of the string. For example, ‘^Ss]2\$’ will match ‘s2’ but not ‘S2f’ or ‘s2s’.

‘.’ – Match any character.

‘**’ – Match the character ‘x’ any number of times, for example ‘x’ will match, as will ‘xxxx’.

‘.*’ – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Diffusion tensor parameter string matching patterns

Please see Table 13.3 on page 262.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Table 13.2: OpenDx mapping types.

Surface type	Name
3D isosurface	'Iso3D'

Table 13.3: Diffusion tensor parameter string matching patterns.

Data type	Object name	Patterns
Global correlation time - τ_m	'tm'	'^tm\$'
Isotropic component of the diffusion tensor - \mathfrak{D}_{iso}	'Diso'	'[Dd]iso'
Anisotropic component of the diffusion tensor - \mathfrak{D}_a	'Da'	'[Dd]a'
Rhombic component of the diffusion tensor - \mathfrak{D}_r	'Dr'	'[Dd]r\$'
Eigenvalue associated with the x-axis of the diffusion tensor - \mathfrak{D}_x	'Dx'	'[Dd]x'
Eigenvalue associated with the y-axis of the diffusion tensor - \mathfrak{D}_y	'Dy'	'[Dd]y'
Eigenvalue associated with the z-axis of the diffusion tensor - \mathfrak{D}_z	'Dz'	'[Dd]z'
Diffusion coefficient parallel to the major axis of the spheroid diffusion tensor - \mathfrak{D}_{\parallel}	'Dpar'	'[Dd]par'
Diffusion coefficient perpendicular to the major axis of the spheroid diffusion tensor - \mathfrak{D}_{\perp}	'Dper'	'[Dd]per'
Ratio of the parallel and perpendicular components of the spheroid diffusion tensor - \mathfrak{D}_{ratio}	'Dratio'	'[Dd]ratio'
The first Euler angle of the ellipsoid diffusion tensor - α	'alpha'	'^a\$' or 'alpha'
The second Euler angle of the ellipsoid diffusion tensor - β	'beta'	'^b\$' or 'beta'
The third Euler angle of the ellipsoid diffusion tensor - γ	'gamma'	'^g\$' or 'gamma'
The polar angle defining the major axis of the spheroid diffusion tensor - θ	'theta'	'theta'
The azimuthal angle defining the major axis of the spheroid diffusion tensor - ϕ	'phi'	'phi'

Table 13.4: Model-free data type string matching patterns.

Data type	Object name
Local τ_m	'local_tm'
Order parameter S^2	's2'
Order parameter S_f^2	's2f'
Order parameter S_s^2	's2s'
Correlation time τ_e	'te'
Correlation time τ_f	'tf'
Correlation time τ_s	'ts'
Chemical exchange	'rex'
CSA	'csa'

Prompt examples

The following commands will generate a map of the extended model-free space for model ‘m5’ consisting of the parameters $\{S^2, S_f^2, \tau_s\}$. Files will be output into the directory ‘dx’ and will be prefixed by ‘map’. In this case, the system is a protein and residue number 6 will be mapped.

```
relax> dx.map(['s2', 's2f', 'ts'], spin_id=':6')

relax> dx.map(['s2', 's2f', 'ts'], spin_id=':6', file_prefix='map', dir='dx')

relax> dx.map(params=['s2', 's2f', 'ts'],
   spin_id=':6', inc=20, file_prefix='map'
   , dir='dx')

relax> dx.map(params=['s2', 's2f', 'ts'],
   spin_id=':6', map_type='Iso3D', inc=20,
   file_prefix='map', dir='dx')
```

To map the model-free space ‘m4’ for residue 2, spin N6 defined by the parameters $\{S^2, \tau_e, R_{ex}\}$, name the results ‘test’, and to place the files in the current directory, use one of the following commands:

```
relax> dx.map(['s2', 'te', 'rex'], spin_id=':2@N6', file_prefix='test', dir=None)

relax> dx.map(params=['s2', 'te', 'rex'],
   spin_id=':2@N6', inc=100, file_prefix='
   test', dir=None)
```

13.2.41 eliminate



Synopsis

Elimination or rejection of models.

Defaults

`eliminate(function=None, args=None)`

Keyword arguments

`function`: An optional user supplied function for model elimination.

`args`: A tuple of arguments used by the optional function for model elimination.

Description

This is used for model validation to eliminate or reject models prior to model selection. Model validation is a part of mathematical modelling whereby models are either accepted or rejected.

Empirical rules are used for model rejection and are listed below. However these can be overridden by supplying a function in the prompt and scripting modes. The function should accept five arguments, a string defining a certain parameter, the value of the parameter, the minimisation instance (ie the residue index if the model is residue specific), and the function arguments. If the model is rejected, the function should return True, otherwise it should return False. The function will be executed multiple times, once for each parameter of the model.

The function arguments should be a tuple, a list enclosed in round brackets, and will be passed to the user supplied function or the inbuilt function. For a description of the arguments accepted by the inbuilt functions, see below.

Once a model is rejected, the select flag corresponding to that model will be set to False so that model selection, or any other function, will then skip the model.

Local tm model elimination rule

The local τ_m , in some cases, may exceed the value expected for a global correlation time. Generally the τ_m value will be stuck at the upper limit defined for the parameter. These models are eliminated using the rule:

`tm >= c`

The default value of `c` is 50 ns, although this can be overridden by supplying the value (in seconds) as the first element of the `args` tuple.

Internal correlation times `te`, `tf`, `ts` model elimination rules

These parameters may experience the same problem as the local τ_m in that the model fails and the parameter value is stuck at the upper limit. These parameters are constrained using the formula ($\tau_e, \tau_f, \tau_s \leq 2\tau_m$). These failed models are eliminated using the rule:

```
te, tf, ts >= c . tm.
```

The default value of `c` is 1.5. Because of round-off errors and the constraint algorithm, setting `c` to 2 will result in no models being eliminated as the minimised parameters will always be less than $2\tau_m$. The value can be changed by supplying the value as the second element of the tuple.

Arguments

The ‘`args`’ argument must be a tuple of length 2, the elements of which must be numbers. For example, to eliminate models which have a local τ_m value greater than 25 ns and models with internal correlation times greater than 1.5 times τ_m , set ‘`args`’ to (25 * 1e-9, 1.5).

13.2.42 fix



Synopsis

Fix or allow parameter values to change during optimisation.

Defaults

```
fix(element=None, fixed=True)
```

Keyword arguments

`element`: Which element to fix.

`fixed`: A flag specifying if the parameters should be fixed or allowed to change.

Description

The element can be any of the following:

‘`diff`’ – The diffusion tensor parameters. This will allow all diffusion tensor parameters to be toggled.

‘`all_spins`’ – Using this keyword, all parameters from all spins will be toggled.

‘`all`’ – All parameters will be toggled. This is equivalent to combining both ‘`diff`’ and ‘`all_spins`’.

The flag ‘`fixed`’, if set to True, will fix parameters during optimisation whereas a value of False will allow parameters to vary.

Prompt examples

13.2.43 frame_order.average-position



Synopsis

Define the mechanics of the average domain position.

Defaults

```
frame_order.average_position(pivot='com', translation=False)
```

Keyword arguments

pivot: The type of pivot to use for the rotation to the average domain position. This can be one of ‘com’ or ‘motional’.

translation: A flag specifying if the average domain position should be allowed to translate during optimisation. If False, then translation can be disabled.

Description

Prior to optimisation, the mechanics of the average moving domain position must be specified. Having the domain shifted to the correct average position is essential for understanding the dynamics as this information is the major contributor to the RDC and PCS. The motional eigenframe (spherical or Euler angles) and ordering (via order parameters, cone angles or torsion angles) come second, and are therefore severely distorted by an incorrect average domain position.

There are two pieces of information affecting this average position - a rotation and translation. For the rotation, a pivot point is required. Note that this pivot is not related to the pivot of the motions. However if you believe that your starting structure lies within the uniform distribution of positions of the domain motions, then the two pivots can be linked by setting the average position pivot to the motional pivot. The default however is to set the pivot to the centre of mass (CoM) of the moving domain.

The second option allows the average domain position to translate during optimisation. By default, only a rotation of the initial structure of the domain is rotated to the average position. But if the rotation is not sufficient to shift the domain to the average position, then a translation will be required. This option will be ignored if no PDC data is present, as RDCs do not contain information about the translation of the domain.

To use the centre of mass as the rotational pivot and to allow translation of the average domain position during optimisation, type one of:

```
relax> frame_order.translate('com', True)
```

```
relax> frame_order.translate(translation=True)
```

```
relax> frame_order.translate(pivot='com', translation=True)
```

To use the motional pivot as the average domain rotational pivot while disallowing translation of, type one of:

```
relax> frame_order.translate('motional')
```

```
relax> frame_order.translate('motional', False)
```

```
relax> frame_order.translate(pivot='motional', translation=False)
```

13.2.44 frame_order.num_int_pts**Synopsis**

Set the number of integration points used in the quasi-random Sobol' sequence during optimisation.

Defaults

```
frame_order.num_int_pts(num=200000)
```

Keyword arguments

num: The number of integration points to use in the Sobol' sequence during optimisation.

Description

This allows the number of integration points used during the Frame Order target function optimisation to be changed from the default. This is used in the quasi-random Sobol' sequence for the numerical integration.

13.2.45 frame_order.pdb_model**Synopsis**

Create a PDB file representation of the frame order dynamics.

Defaults

```
frame_order.pdb_model(ave_pos_file='ave_pos.pdb',
                      rep_file='frame_order.pdb',
                      dist_file='domain_distribution.pdb',
                      dir=None,
                      size=30.0,
                      inc=36,
                      force=False)
```

Keyword arguments

ave_pos_file: The name of the 3D structure PDB file for the molecular structure with the moving domains shifted to the average position.

rep_file: The name of the PDB file for the geometric object representation of the frame order dynamics.

dist_file: The name of the file which will contain multiple models spanning the full dynamics distribution of the frame order model.

dir: The directory where the file is to be located.

size: The size of the geometric object in Å.

inc: The number of increments used to create the geometric object.

force: A flag which, if set to True, will overwrite the any pre-existing files.

Description

This function creates a PDB file containing an artificial geometric structure representing the Frame Order cone models.

There are four different types of residue within the PDB. The pivot point is represented as a single carbon atom of the residue 'PIV'. The cone consists of numerous H atoms of the residue 'CON'. The cone axis vector is presented as the residue 'AXE' with one carbon atom positioned at the pivot and the other x Å away on the cone axis (set by the geometric object size). Finally, if Monte Carlo have been performed, there will be multiple 'MCC' residues representing the cone for each simulation, and multiple 'MCA' residues representing the multiple cone axes.

To create the diffusion in a cone PDB representation, a uniform distribution of vectors on a sphere is generated

using spherical coordinates with the polar angle defined by the cone axis. By incrementing the polar angle using an arccos distribution, a radial array of vectors representing latitude are created while incrementing the azimuthal angle evenly creates the longitudinal vectors. These are all placed into the PDB file as H atoms and are all connected using PDB CONECT records. Each H atom is connected to its two neighbours on the both the longitude and latitude. This creates a geometric PDB object with longitudinal and latitudinal lines representing the filled cone.

13.2.46 frame_order.pivot



Synopsis

Set the pivot point for the two body motion in the structural coordinate system.

Defaults

`frame_order.pivot(pivot=None, fix=None)`

Keyword arguments

`pivot`: The pivot point for the motion (e.g. the position between the 2 domains in PDB coordinates).

`fix`: A flag specifying if the pivot point should be fixed during optimisation.

Description

This will set the pivot point for the two domain system within the PDB coordinate system. This is required for interpreting PCS data as well as for the generation of cone or other PDB representations of the domain motions.

Prompt examples

To set the pivot point, type one of:

```
relax> frame_order.pivot([12.067, 14.313, -3  
.2675])
```

```
relax> frame_order.pivot(pivot=[12.067, 14  
.313, -3.2675])
```

13.2.47 frame_order.quad_int**Synopsis**

Turn the high precision quadratic integration on or off.

Defaults

`frame_order.quad_int(flag=False)`

Keyword arguments

`flag`: The flag with if True will perform high precision numerical integration via the `scipy.integrate quad()`, `dblquad()` and `tplquad()` integration methods rather than the rough quasi-random numerical integration.

Description

This allows the high precision numerical integration of the Scipy `quad()` and related functions to be used instead of the lower precision quasi-random Sobol' sequence integration. This is for the optimisation of the Frame Order target functions. The quadratic integration is orders of magnitude slower than the Sobol' sequence integration, but the precision is much higher.

13.2.48 frame_order.ref_domain**Synopsis**

Set the reference domain for the ‘2-domain’ Frame Order theories.

Defaults

`frame_order.ref_domain(ref=None)`

Keyword arguments

`ref`: The domain which will act as the frame of reference. This is only valid for the ‘2-domain’ Frame Order theories.

Description

Prior to optimisation of the ‘2-domain’ Frame Order theories, which of the two domains will act as the frame of reference must be specified. This is important for the attachment of cones to domains, etc.

Prompt examples

To set up the isotropic cone frame order model with ‘centre’ domain being the frame of reference, type:

`relax> frame_order.ref_domain(ref='centre')`

13.2.49 frame_order.select_model



Synopsis

Select and set up the Frame Order model.

Defaults

```
frame_order.select_model(model=None)
```

Keyword arguments

`model`: The name of the preset Frame Order model.

Description

Prior to optimisation, the Frame Order model should be selected. These models consist of three parameter categories:

The average domain position. This includes the parameters `ave_pos_alpha`, `ave_pos_beta`, and `ave_pos_gamma`. These Euler angles rotate the tensors from the arbitrary PDB frame of the moving domain to the average domain position.

The frame order eigenframe. This includes the parameters `eigen_alpha`, `eigen_beta`, and `eigen_gamma`. These Euler angles define the major modes of motion. The cone central axis is defined as the z-axis. The pseudo-elliptic cone x and y-axes are defined as the x and y-axes of the eigenframe.

The cone parameters. These are defined as the tilt-torsion angles `cone_theta_x`, `cone_theta_y`, and `cone_sigma_max`. The `cone_theta_x` and `cone_theta_y` parameters define the two cone opening angles of the pseudo-ellipse. The amount of domain torsion is defined as the average domain position, plus and minus `cone_sigma_max`. The isotropic cones are defined by setting `cone_theta_x = cone_theta_y` and converting the single parameter into a 2nd rank order parameter.

The list of available models are:

‘pseudo-ellipse’ – The pseudo-elliptic cone model. This is the full model consisting of the parameters `ave_pos_alpha`, `ave_pos_beta`, `ave_pos_gamma`, `eigen_alpha`, `eigen_beta`, `eigen_gamma`, `cone_theta_x`, `cone_theta_y`, and `cone_sigma_max`.

‘pseudo-ellipse, torsionless’ – The pseudo-elliptic cone with the torsion angle `cone_sigma_max` set to zero.

‘pseudo-ellipse, free rotor’ – The pseudo-elliptic cone with no torsion angle restriction.

‘iso cone’ – The isotropic cone model. The cone is defined by a single order parameter `s1` which is related to the single cone opening angle `cone_theta_x = cone_theta_y`. Due to rotational symmetry about the cone axis, the average position α Euler angle `ave_pos_alpha` is dropped from the model. The symmetry also collapses the eigenframe to a single z-axis defined by the parameters `axis_theta` and `axis_phi`.

‘iso cone, torsionless’ – The isotropic cone model with the torsion angle `cone_sigma_max` set to zero.

‘iso cone, free rotor’ – The isotropic cone model with no torsion angle restriction.

‘line’ – The line cone model. This is the pseudo-elliptic cone with one of the cone angles, `cone_theta_y`, assumed to be statistically negligible. I.e. the cone angle is so small that it cannot be distinguished from noise.

‘line, torsionless’ – The line cone model with the torsion angle `cone_sigma_max` set to zero.

‘line, free rotor’ – The line cone model with no torsion angle restriction.

‘rotor’ – The only motion is a rotation about the cone axis restricted by the torsion angle `cone_sigma_max`.

‘rigid’ – No domain motions.

‘free rotor’ – The only motion is free rotation about the cone axis.

Prompt examples

To select the isotropic cone model, type:

```
relax> frame_order.select_model(model='iso
cone')
```

13.2.50 grace.view

 Grace

Synopsis

Visualise the file within Grace.

Defaults

```
grace.view(file=None, dir='grace', grace_exe='xmgrace')
```

Keyword arguments

file: The name of the file.

dir: The directory name.

grace_exe: The Grace executable file.

Description

This can be used to view the specified Grace ‘*.agr’ file by opening it with the Grace program.

Prompt examples

To view the file ‘s2.agr’ in the directory ‘grace’, type:

```
relax> grace.view(file='s2.agr')
```

```
relax> grace.view(file='s2.agr', dir='grace'
    )
```

13.2.51 grace.write

 Grace

 Grace



Synopsis

Create a grace ‘*.agr’ file to visualise the 2D data.

Defaults

```
grace.write(x_data_type='res_num', y_data_type=None,
spin_id=None, plot_data='value', file=None, dir='grace',
force=False, norm=False)
```

Keyword arguments

x_data_type: The data type for the X-axis (no regular expression is allowed).

y_data_type: The data type for the Y-axis (no regular expression is allowed).

spin_id: The spin ID string.

plot_data: The data to use for the plot.

file: The name of the file.

dir: The directory name.

force: A flag which, if set to True, will cause the file to be overwritten.

norm: A flag which, if set to True, will cause all graphs to be normalised to a starting value of 1. This is for the normalisation of series type data.

Description

This is designed to be as flexible as possible so that any combination of data can be plotted. The output is in the format of a Grace plot (also known as ACE/gr, Xmgr, and xmgrace) which only supports two dimensional plots. Three types of information can be used to create various types of plot. These include the x-axis and y-axis data types, the spin ID string, and the type of data plot.

The x-axis and y-axis data types should be plain strings, regular expression is not allowed. The two axes of the Grace plot can be any of the data types listed in the tables below. The only limitation is that the data must belong to the same data pipe.

If the x-axis data type is not given, the plot will default to having the residue numbering along the x-axis. Two special data types for the axes are:

'res_num' – The axis will consist of the residue numbering.

'spin_num' – The axis will consist of the spin numbering.

The spin ID string can be used to limit which spins are used in the plot. The default is that all spins will be used, however, the ID string can be used to select a subset of all spins, or a single spin for plots of Monte Carlo simulations, etc.

The property which is actually plotted can be controlled by the plot data setting. This can be one of the following:

'value' – Plot values (with errors if they exist).

'error' – Plot errors.

'sims' – Plot the simulation values.

Normalisation is only allowed for series type data, for example the R₂ exponential curves, and will be ignored for all other data types. If the norm flag is set to True then the y-value of the first point of the series will be set to 1. This normalisation is useful for highlighting errors in the data sets.

Regular expression

The python function '`match`', which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

'[]' – A sequence or set of characters to match to a single character. For example, '[ss]2' will match both 'S2' and 's2'.

'^' – Match the start of the string.

'\$' – Match the end of the string. For example, '^Ss]2\$' will match 's2' but not 'S2f' or 's2s'.

'.' – Match any character.

''** – Match the character 'x' any number of times, for example 'x' will match, as will 'xxxx'.

'.*' – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Minimisation statistic data type string matching patterns

Please see Table 13.5 on page 272.

NOE calculation data type string matching patterns

Please see Table 13.6 on page 272.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Prompt examples

To write the NOE values for all spins to the Grace file '`noe.agr`', type one of:

```
relax> grace.write('res_num', 'noe', file='noe.agr')
```

```
relax> grace.write(y_data_type='noe', file='noe.agr')
```

```
relax> grace.write(x_data_type='res_num',
y_data_type='noe', file='noe.agr')
```

```
relax> grace.write(y_data_type='noe', file='noe.agr',
force=True)
```

To create a Grace file of 's2' vs. 'te' for all spins, type one of:

```
relax> grace.write('s2', 'te', file='s2_te.agr')
```

Table 13.5: Minimisation statistic data type string matching patterns.

Data type	Object name	Patterns
Chi-squared statistic	'chi2'	'^[[Cc]hi2\$' or '^[[Cc]hi[-][Ss]quare'
Iteration count	'iter'	'^[[Ii]ter'
Function call count	'f_count'	'^[[Ff].*[-_][Cc]ount'
Gradient call count	'g_count'	'^[[Gg].*[-_][Cc]ount'
Hessian call count	'h_count'	'^[[Hh].*[-_][Cc]ount'

Table 13.6: NOE data type string matching patterns.

Data type	Object name
Reference intensity	'ref'
Saturated intensity	'sat'
NOE	'noe'

Table 13.7: Relaxation curve fitting data type string matching patterns.

Data type	Object name
Relaxation rate	'rx'
Peak intensities (series)	'intensities'
Initial intensity	'i0'
Intensity at infinity	'iinf'
Relaxation period times (series)	'relax_times'

Table 13.8: Reduced spectral density mapping data type string matching patterns.

Data type	Object name
$J(0)$	'j0'
$J(\omega_X)$	'jwx'
$J(\omega_H)$	'jwh'
CSA	'csa'

Table 13.9: Consistency testing data type string matching patterns.

Data type	Object name
$J(0)$	'j0'
F_eta	'f_eta'
F_R2	'f_r2'
Bond length	'r'
CSA	'csa'
Heteronucleus type	'heteronuc_type'
Proton type	'proton_type'
Angle θ	'orientation'
Correlation time	'tc'

```
relax> grace.write(x_data_type='s2',
    y_data_type='te', file='s2_te.agr')
```

```
relax> grace.write(x_data_type='s2',
    y_data_type='te', file='s2_te.agr',
    force=True)
```

To create a Grace file of the Monte Carlo simulation values of ‘rex’ vs. ‘te’ for residue 123, type one of:

```
relax> grace.write('rex', 'te', spin_id='
    :123', plot_data='sims', file='
    s2_te.agr')
```

```
relax> grace.write(x_data_type='rex',
    y_data_type='te', spin_id=':123',
    plot_data='sims', file='s2_te.agr')
```

By plotting the peak intensities, the integrity of exponential relaxation curves can be checked and anomalies searched for prior to model-free analysis or reduced spectral density mapping. For example the normalised average peak intensities can be plotted versus the relaxation time periods for the relaxation curves of all residues of a protein. The normalisation, whereby the initial peak intensity of each residue I(0) is set to 1, emphasises any problems. To produce this Grace file, type:

```
relax> grace.write(x_data_type='relax_times'
    , y_data_type='ave_int', file='
    intensities_norm.agr', force=True, norm
    =True)
```

13.2.52 grid_search



Synopsis

Perform a grid search.

Defaults

```
grid_search(lower=None, upper=None, inc=21,
constraints=True, verbosity=1)
```

Keyword arguments

lower: An array of the lower bound parameter values for the grid search. The length of the array should be equal to the number of parameters in the model.

upper: An array of the upper bound parameter values for the grid search. The length of the array should be equal to the number of parameters in the model.

inc: The number of increments to search over. If a single integer is given then the number of increments will be equal in all dimensions. Different numbers of increments in each direction can be set if ‘inc’ is set to an array of integers of length equal to the number of parameters.

constraints: A boolean flag specifying whether the parameters should be constrained. The default is to turn constraints on (constraints=True).

verbosity: The amount of information to print to screen. Zero corresponds to minimal output while higher values increase the amount of output. The default value is 1.

Description

This will perform a grid search across the parameter space.

13.2.53 interatom.copy



Synopsis

Copy all data associated with a interatomic data container.

Defaults

```
interatom.copy(pipe_from=None, pipe_to=None,
spin_id1=None, spin_id2=None)
```

Keyword arguments

pipe_from: The data pipe containing the interatomic data container from which the data will be copied. This defaults to the current data pipe.

pipe_to: The data pipe to copy the interatomic data container to. This defaults to the current data pipe.

spin_id1: The spin ID of the first spin.

spin_id2: The spin ID of the second spin.

Description

This will copy all the data associated with the identified interatomic data container to a different data pipe. The new interatomic data container must not already exist.

Prompt examples

To copy the interatomic data container between ‘:2@C’ and ‘:2@H’, from the ‘orig’ data pipe to the current data pipe, type one of:

```
relax> interatom.copy('orig', spin_id1=':2@C'
 $\quad$  , spin_id2=':2@H')
```

```
relax> interatom.copy(pipe_from='orig',
 $\quad$  spin_id1=':2@C', spin_id2=':2@H')
```



13.2.54 interatom.define



Synopsis

Define interatomic interactions between pairs of spins.

Defaults

```
interatom.define(spin_id1='@N', spin_id2='@H',
direct_bond=True, pipe=None)
```

Keyword arguments

spin_id1: The spin ID string for the first spin of the interatomic interaction.

spin_id2: The spin ID string for the second spin of the interatomic interaction.

direct_bond: This is a flag which if True means that the two spins are directly bonded. This flag is useful to simplify the set up of the main heteronuclear relaxation mechanism or one-bond residual dipolar couplings.

pipe: The data pipe to create the interatomic data container for. This defaults to the current data pipe if not supplied.

Description

To analyse relaxation or residual dipolar coupling (RDC) data, for example, pairs of spins which are coupled need to be defined. This can be via the magnetic dipole-dipole interaction or scalar coupling interaction. This function will create an interatomic data object connecting two existing spins. This data container will be used to store all information about the interactomic interaction including interatomic vectors and distances.

For analyses which use relaxation data, simply defining the interatomic interaction will indicate that there is a dipolar relaxation mechanism operating between the two spins. Note that for model-free analyses or reduced spectral density mapping, only a single relaxation mechanism can be handled. For RDC dependent analyses, the presence of the interatomic interaction indicates that dipolar coupling is expected between the two spins.

Prompt examples

To connect the spins ‘:1@N’ to ‘:1@H’, type one of:

```
relax> interatom.define(':1@N', ':1@H')
```

```
relax> interatom.define(spin_id1=':1@N',
    spin_id2=':1@H')
```

To define the protein 15N heteronuclear relaxation mechanism for a model-free analysis, type one of the following:

```
relax> interatom.define('@N', '@H', True)
```

```
relax> interatom.define(spin_id1='@N',
    spin_id2='@H', direct_bond=True)
```

13.2.55 interatom.read_dist



Synopsis

Read inter-spin distances from a file.

Defaults

```
interatom.read_dist(file=None, dir=None, unit='meter',
spin_id1_col=1, spin_id2_col=2, data_col=3, sep=None)
```

Keyword arguments

file: The name of the file containing the averaged distance data.

dir: The directory where the file is located.

unit: The unit of distance. The default is meter, but Å can also be specified.

spin_id1_col: The spin ID string column for the first spin.

spin_id2_col: The spin ID string column for the second spin.

data_col: The distance data column.

sep: The column separator (the default is white space).

Description

This allows interatomic distances to be read from a file. This is useful in the case when the distances vary, avoiding having to tediously use the interatom.set_dist user function for each spin-pair separately. The format of the file should be columnar, with the two spin ID strings in two separate columns and the distances in any other. The default measurement unit is meter but this can be changed to Å.

For RDC and relaxation based analyses, as the magnetic dipole-dipole interaction is averaged in NMR over the interatomic distance to the inverse third power, the interatomic distances within a 3D structural file are of no use for defining the interaction. Therefore these r^{-3} average distances must be explicitly defined.

Prompt examples

To load the distances in meters from the fifth column of the ‘distances’ file, and where the spin IDs are in the first and second columns, type one of the following:

```
relax> interatom.read_dist('distances', 1,
    2, 5)
```

```
relax> interatom.read_dist(file='distances',
    unit='meter', spin_id1_col=1,
    spin_id2_col=2, data_col=5)
```

13.2.56 interatom.set_dist



Synopsis

Set the inter-spin distances.

Defaults

```
interatom.set_dist(spin_id1='@N', spin_id2='@H',
ave_dist=1.0200000000000001e-10, unit='meter')
```

Keyword arguments

spin_id1: The spin identification string for the first spin of the dipole pair.

spin_id2: The spin identification string for the second spin of the dipole pair.

ave_dist: The r^{-3} averaged distance between the two spins to be used in the magnetic dipole constant, defaulting to meters.

unit: The unit of distance (the default is ‘meter’).

Description

For many NMR interactions, the distance between the spin of interest and another spin or atom must be defined. This information can be extracted from a 3D structure but, in many cases, these distances are not of interest. For example the empirical or fixed distance calculation of proton positions in X-ray crystallographic structures will often not correspond to the real interatomic distances.

Another example is the magnetic dipole-dipole interaction which is averaged over the interatomic distance to the inverse third power. In this case, the interatomic distances from any 3D structural file can be of no use for defining the interaction. The average distances must be explicitly supplied. This user function allows these distances to be set up. The default measurement unit is meter but this can be changed to Å. Alternatively the distances can be read from a file using other user functions in this class.

Prompt examples

To set the N-H distance for protein the ¹⁵N heteronuclear relaxation mechanism to 1.02 Å, type one of the following:

```
relax> interatom.set_dist('@N', '@H', 1.02 *
    1e-10)
```

```
relax> interatom.set_dist(spin_id1='@N',
    spin_id2='@H', ave_dist=1.02 * 1e-10,
    unit='meter')

relax> interatom.set_dist(spin_id1='@N',
    spin_id2='@H', ave_dist=1.02, unit='
Angstrom')
```

13.2.57 interatom.unit_vectors



Synopsis

Calculate the unit vectors for all interatomic interactions.

Defaults

```
interatom.unit_vectors(ave=True)
```

Keyword arguments

ave: A flag which if True will cause the bond vectors from all models to be averaged. If vectors from only one model is extracted, this will have no effect.

Description

For an orientational dependent analysis, such as model-free analysis with the spheroidal and ellipsoidal global diffusion tensors or any analysis using RDCs, the unit vectors between the two dipoles must be calculated prior to starting the analysis. For the unit vector extraction, the two interacting spins should already possess positional information and the dipole-dipole interaction should already be defined via the interatom.define user function. This information will be used to calculate unit vectors between the two spins. Without positional information, no vectors can be calculated and an orientational dependent analysis will not be possible.

The number of unit vectors per interaction will be defined by the number of positions each spin possesses together with the averaging flag. If both spins have N and M positions loaded, the number of positions for both must match ($N=M$). In this case, as well as when one spin has N positions and the other a single position, then N unit vectors will be calculated. This is unless the averaging flag is set in which case an averaged vector of unit length will be calculated.

Prompt examples

To calculate the unit vectors prior to a model-free analysis, type one of the following:

```
relax> interatom.unit_vectors(True)
```

```
relax> interatom.unit_vectors(ave=True)
```

13.2.58 j_coupling.copy**Synopsis**

Copy J coupling data from one data pipe to another.

Defaults

`j_coupling.copy(pipe_from=None, pipe_to=None)`

Keyword arguments

`pipe_from`: The name of the pipe to copy the J coupling data from.

`pipe_to`: The name of the pipe to copy the J coupling data to.

Description

This function will copy J coupling data from one pipe to another.

Prompt examples

To copy all J coupling data from pipe ‘DMSO’ to pipe ‘CDC13’, type one of:

```
relax> j_coupling.copy('DMSO', 'CDC13')
```

```
relax> j_coupling.copy(pipe_from='DMSO',
    pipe_to='CDC13')
```

13.2.59 j_coupling.delete**Synopsis**

Delete the J coupling values.

Defaults

`j_coupling.delete()`

Description

This will delete all J coupling data in the current data pipe.

Prompt examples

To delete all J coupling data, type:

```
relax> j_coupling.delete()
```



13.2.60 j_coupling.display



Synopsis

Display the J coupling data in the current data pipe.

Defaults

`j_coupling.display()`

Description

This will display all of the J coupling data in the current data pipe.

Prompt examples

To display all J coupling data, type:

```
relax> j_coupling.display()
```

13.2.61 j_coupling.read



Synopsis

Read the J coupling data from file.

Defaults

`j_coupling.read(file=None, dir=None, spin_id1_col=1, spin_id2_col=2, data_col=None, error_col=None, sign_col=None, sep=None)`

Keyword arguments

`file`: The name of the file containing the J coupling data.

`dir`: The directory where the file is located.

`spin_id1_col`: The spin ID string column for the first spin.

`spin_id2_col`: The spin ID string column for the second spin.

`data_col`: The J coupling data column.

`error_col`: The experimental error column.

`sign_col`: A special column holding the sign of the J coupling, being either 1 or -1, in case this data is obtained separately.

`sep`: The column separator (the default is white space).

Description

This will read J coupling data from a file. If the sign of the J coupling has been determined by a different experiment, this information can be present in a different column having either the value of 1 or -1.

Prompt examples

The following commands will read the J coupling data out of the file 'J.txt' where the columns are separated by the symbol ',':

```
relax> j_coupling.read('J.txt', sep=',')
```

If the individual spin J coupling errors are located in the file 'j_err.txt' in column number 5 then, to read these values into relax, type one of:

```
relax> j_coupling.read('j_err.txt',
    error_col=5)

relax> j_coupling.read(file='j_err.txt',
    error_col=5)
```

13.2.62 j_coupling.write



Synopsis

Write the J coupling data to file.

Defaults

```
j_coupling.write(file=None, dir=None, force=False)
```

Keyword arguments

file: The name of the file.

dir: The directory name.

force: A flag which if True will cause the file to be overwritten.

Description

This will write the J coupling values to file. If no directory name is given, the file will be placed in the current working directory.

13.2.63 jw_mapping.set_frq

 $J(\omega)$ ω

Synopsis

Select which relaxation data to use in the $J(\omega)$ mapping by NMR spectrometer frequency.

Defaults

```
jw_mapping.set_frq(frq=None)
```

Keyword arguments

frq: The spectrometer frequency in Hz. This must match the currently loaded data to the last decimal point. See the ‘`sfrq`’ parameter in the Varian propar file or the ‘`SF01`’ parameter in the Bruker acqus file.

Description

This will select the relaxation data to use in the reduced spectral density mapping corresponding to the given frequency. The data is selected by the spectrometer frequency in Hertz, which should be set to the exact value (see the ‘`sfrq`’ parameter in the Varian propar file or the ‘`SF01`’ parameter in the Bruker acqus file). Note though that the R_1 , R_2 and NOE are all expected to have the exact same frequency in the $J(\omega)$ mapping analysis (to the last decimal point).

Prompt examples

```
relax> jw_mapping.set_frq(600.0 * 1e6)
```

```
relax> jw_mapping.set_frq(frq=600.0 * 1e6)
```

13.2.64 minimise



Synopsis

Perform an optimisation.

Defaults

```
minimise(min_algor='newton', line_search=None,
hessian_mod=None, hessian_type=None, func_tol=1e-25,
grad_tol=None, max_iter=10000000, constraints=True,
scaling=True, verbosity=1)
```

Keyword arguments

min_algor: The optimisation algorithm to use.

line_search: The line search algorithm which will only be used in combination with the line search and conjugate gradient methods. This will default to the More and Thuente line search.

hessian_mod: The Hessian modification. This will only be used in the algorithms which use the Hessian, and defaults to Gill, Murray, and Wright modified Cholesky algorithm.

hessian_type: The Hessian type. This will only be used in a few trust region algorithms, and defaults to BFGS.

func_tol: The function tolerance. This is used to terminate minimisation once the function value between iterations is less than the tolerance. The default value is `1e-25`.

grad_tol: The gradient tolerance. Minimisation is terminated if the current gradient value is less than the tolerance. The default value is `None`.

max_iter: The maximum number of iterations. The default value is `1e7`.

constraints: A boolean flag specifying whether the parameters should be constrained. The default is to turn constraints on (`constraints=True`).

scaling: The diagonal scaling boolean flag. The default that scaling is on (`scaling=True`).

verbosity: The amount of information to print to screen. Zero corresponds to minimal output while higher values increase the amount of output. The default value is `1`.

Description

This will perform an optimisation starting from the current parameter values. This is only suitable for data pipe types which have target functions and hence support optimisation.

Diagonal scaling

Diagonal scaling is the transformation of parameter values such that each value has a similar order of magnitude. Certain minimisation techniques, for example the trust region methods, perform extremely poorly with badly scaled problems. In addition, methods which are insensitive to scaling such as Newton minimisation may still benefit due to the minimisation of round off errors.

In Model-free analysis for example, if $S^2 = 0.5$, $\tau_e = 200$ ps, and $R_{ex} = 15$ 1/s at 600 MHz, the unscaled parameter vector would be [0.5, 2.0e-10, 1.055e-18]. R_{ex} is divided by $(2 * \pi * 600,000,000)^{**2}$ to make it field strength independent. The scaling vector for this model may be something like [1.0, 1e-9, $1/(2 * \pi * 6e8)^{**2}$]. By dividing the unscaled parameter vector by the scaling vector the scaled parameter vector is [0.5, 0.2, 15.0]. To revert to the original unscaled parameter vector, the scaled parameter vector and scaling vector are multiplied.

Minimisation algorithms

A minimisation function is selected if the minimisation algorithm matches a certain pattern. Because the python regular expression ‘`match`’ statement is used, various strings can be supplied to select the same minimisation algorithm. Below is a list of the minimisation algorithms available together with the corresponding patterns.

This is a short description of python regular expression, for more information, see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

- ‘[]’ – A sequence or set of characters to match to a single character. For example, ‘[Nn]ewton’ will match both ‘Newton’ and ‘newton’.
- ‘^’ – Match the start of the string.
- ‘\$’ – Match the end of the string. For example, ‘^L1] [Mm]\$’ will match ‘1m’ and ‘LM’ but will not match if characters are placed either before or after these strings.

To select a minimisation algorithm, use a string which matches one of the following patterns given in the tables.

Unconstrained line search methods:

Please see Table 13.10 on page 283.

Unconstrained trust-region methods:

Please see Table 13.11 on page 283.

Unconstrained conjugate gradient methods:

Please see Table 13.12 on page 283.

Miscellaneous unconstrained methods:

Please see Table 13.13 on page 283.

Global minimisation methods:

Please see Table 13.14 on page 283.

Minimisation options

The minimisation options can be given in any order.

Line search algorithms. These are used in the line search methods and the conjugate gradient methods. The default is the Backtracking line search. The algorithms are:

Please see Table 13.15 on page 284.

Hessian modifications. These are used in the Newton, Dogleg, and Exact trust region algorithms:

Please see Table 13.16 on page 284.

Hessian type, these are used in a few of the trust region methods including the Dogleg and Exact trust region algorithms. In these cases, when the Hessian type is set to Newton, a Hessian modification can also be supplied as above. The default Hessian type is Newton, and the default Hessian modification when Newton is selected is the GMW algorithm:

Please see Table 13.17 on page 284.

For Newton minimisation, the default line search algorithm is the More and Thuente line search, while the default Hessian modification is the GMW algorithm.

Prompt examples

To apply Newton minimisation together with the GMW81 Hessian modification algorithm, the More and Thuente line search algorithm, a function tolerance of 1e-25, no gradient tolerance, a maximum of 10,000,000 iterations, constraints turned on to limit parameter values, and have normal printout, type any combination of:

```
relax> minimise('newton')
relax> minimise('Newton')
relax> minimise('newton', 'gmw')
relax> minimise('newton', 'mt')
relax> minimise('newton', 'gmw', 'mt')
relax> minimise('newton', 'mt', 'gmw')
relax> minimise('newton', func_tol=1e-25)
```

Table 13.10: Minimisation algorithms – unconstrained line search methods.

Minimisation algorithm	Patterns
Back-and-forth coordinate descent	'^[[Cc][Dd]\$' or '^[[Cc]oordinate[-][Dd]escent\$'
Steepest descent	'^[[Ss][Dd]\$' or '^[[Ss]teepest[-][Dd]escent\$'
Quasi-Newton BFGS	'^[[Bb][Ff][Gg][Ss]\$'
Newton	'^[[Nn]ewton\$'
Newton-CG	'^[[Nn]ewton[-][Cc][Gg]\$' or '^[[Nn][Cc][Gg]\$'

Table 13.11: Minimisation algorithms – unconstrained trust-region methods.

Minimisation algorithm	Patterns
Cauchy point	'^[[Cc]auchy'
Dogleg	'^[[Dd]ogleg'
CG-Steihaug	'^[[Cc][Gg][-_-][Ss]teihaug' or '^[[Ss]teihaug'
Exact trust region	'^[[Ee]xact'

Table 13.12: Minimisation algorithms – unconstrained conjugate gradient methods.

Minimisation algorithm	Patterns
Fletcher-Reeves	'^[[Ff][Rr]\$' or '^[[Ff]letcher[-_-][Rr]eeves\$'
Polak-Ribiere	'^[[Pp][Rr]\$' or '^[[Pp]olak[-_-][Rr]ibiere\$'
Polak-Ribière +	'^[[Pp][Rr]\+\$' or '^[[Pp]olak[-_-][Rr]ibiere\+\$'
Hestenes-Stiefel	'^[[Hh][Ss]\$' or '^[[Hh]estenes[-_-][Ss]tiefel\$'

Table 13.13: Minimisation algorithms – miscellaneous unconstrained methods.

Minimisation algorithm	Patterns
Simplex	'^[[Ss]implex\$'
Levenberg-Marquardt	'^[[Ll][Mm]\$' or '^[[Ll]evenburg-[Mm]arquardt\$'

Table 13.14: Minimisation algorithms – global minimisation methods.

Minimisation algorithm	Patterns
Simulated Annealing	'^[[Ss][Aa]\$' or '^[[Ss]imulated [Aa]nnealing\$'

Table 13.15: Minimisation sub-algorithms – line search algorithms.

Line search algorithm	Patterns
Backtracking line search	'^[[Bb]ack'
Nocedal and Wright interpolation based line search	'^[[Nn][Ww][Ii]' or '^[[Nn]ocedal[_][Ww]right[_][Ii]nt'
Nocedal and Wright line search for the Wolfe conditions	'^[[Nn][Ww][Ww]' or '^[[Nn]ocedal[_][Ww]right[_][Ww]olfe'
More and Thuente line search	'^[[Mm][Tt]' or '^[[Mm]ore[_][Tt]huente\$'
No line search	'^[[Nn]o [Ll]ine [Ss]earch\$'

Table 13.16: Minimisation sub-algorithms – Hessian modifications.

Hessian modification	Patterns
Unmodified Hessian	'^[[Nn]o [Hh]essian [Mm]od'
Eigenvalue modification	'^[[Ee]igen'
Cholesky with added multiple of the identity	'^[[Cc]hol'
The Gill, Murray, and Wright modified Cholesky algorithm	'^[[Gg][Mm][Ww]\$'
The Schnabel and Eskow 1999 algorithm	'^[[Ss][Ee]99'

Table 13.17: Minimisation sub-algorithms – Hessian type.

Hessian type	Patterns
Quasi-Newton BFGS	'^[[Bb][Ff][Gg][Ss]\$'
Newton	'^[[Nn]ewton\$'

```
relax> minimise('newton', func_tol=1e-25,
                 grad_tol=None)

relax> minimise('newton', max_iter=1e7)

relax> minimise('newton', constraints=True,
                 max_iter=1e7)

relax> minimise('newton', verbosity=1)
```

To use constrained Simplex minimisation with a maximum of 5000 iterations, type:

```
relax> minimise('simplex', constraints=True,
                 max_iter=5000)
```

13.2.65 model_free.create_model

S^2, τ_e



Synopsis

Create a model-free model.

Defaults

```
model_free.create_model(model=None, equation=None,
                        params=None, spin_id=None)
```

Keyword arguments

model: The new name of the model-free model.

equation: The model-free equation.

params: The array of parameter names of the model.

spin_id: The spin identification string.

Description

This user function should almost never be used. It is provided for academic reasons for the study of old analyses and published results. If you are looking for a normal model-free model, use the `model_free.select_model` user function instead.

Model-free equation

The model-free equation can be one of the following:

‘mf_orig’ selects the original model-free equations with parameters $\{S^2, \tau_e\}$.

‘mf_ext’ selects the extended model-free equations with parameters $\{S_f^2, \tau_f, S^2, \tau_s\}$.

‘mf_ext2’ selects the extended model-free equations with parameters $\{S_f^2, \tau_f, S_s^2, \tau_s\}$.

Model-free parameters

The following parameters are accepted for the original model-free equation:

‘s2’ – The square of the generalised order parameter.

‘te’ – The effective correlation time.

The following parameters are accepted for the extended model-free equation:

‘s2f’ – The square of the generalised order parameter of the faster motion.

‘tf’ – The effective correlation time of the faster motion.

‘s2’ – The square of the generalised order parameter $S^2 = S_f^2 * S_s^2$.

‘ts’ – The effective correlation time of the slower motion.

The following commands will create the model-free model ‘large_model’ which is based on the extended model-free equation and contains the seven parameters ‘s2f’, ‘tf’, ‘s2’, ‘ts’, ‘rex’, ‘csa’, ‘r’.

```
relax> model_free.create_model('large_model'
, 'mf_ext', ['s2f', 'tf', 's2', 'ts',
'rex', 'csa', 'r'])
```

```
relax> model_free.create_model(model='large_model',
params=['s2f', 'tf', 's2',
'ts', 'rex', 'csa', 'r'], equation='mf_ext')
```

The following parameters are accepted for the extended 2 model-free equation:

‘s2f’ – The square of the generalised order parameter of the faster motion.

‘tf’ – The effective correlation time of the faster motion.

‘s2s’ – The square of the generalised order parameter of the slower motion.

‘ts’ – The effective correlation time of the slower motion.

The following parameters are accepted for all equations:

‘rex’ – The chemical exchange relaxation.

‘r’ – The average bond length $\langle r \rangle$.

‘csa’ – The chemical shift anisotropy.

Spin identification string

If ‘spin_id’ is supplied then the model will only be created for the corresponding spins. Otherwise the model will be created for all spins.

Prompt examples

The following commands will create the model-free model ‘m1’ which is based on the original model-free equation and contains the single parameter ‘s2’.

```
relax> model_free.create_model('m1',
'mf_orig', ['s2'])
```

```
relax> model_free.create_model(model='m1',
params=['s2'], equation='mf_orig')
```

13.2.66 model_free.delete S^2, τ_e **Synopsis**

Delete all model-free data from the current data pipe.

Defaults**model_free.delete()****Description**

This will delete all of the model-free data - parameters, model, etc. - from the current data pipe.

Prompt examples

To delete all model-free data, type:

```
relax> model_free.delete()
```

13.2.67 model_free.remove_tm S^2, τ_e **Synopsis**Remove the local τ_m parameter from a model.**Defaults****model_free.remove_tm(spin_id=None)****Keyword arguments**

spin_id: The spin identification string.

Description

This function will remove the local τ_m parameter from the model-free parameter set. If there is no local τ_m parameter within the set nothing will happen.

If no spin identification string is given, then the function will apply to all spins.

Prompt examples

The following command will remove the parameter ‘tm’:

```
relax> model_free.remove_tm()
```

13.2.68 model_free.select_model

S^2, τ_e



Synopsis

Select a preset model-free model.

Defaults

model_free.select_model(model=None, spin_id=None)

Keyword arguments

model: The name of the preset model.

spin_id: The spin identification string.

Description

This allows a standard model-free model to be selected from a long list of models.

The preset models

The standard preset model-free models are

‘m0’ – {},

‘m1’ – {S2},

‘m2’ – { S^2, τ_e },

‘m3’ – { S^2, R_{ex} },

‘m4’ – { S^2, τ_e, R_{ex} },

‘m5’ – { S_f^2, S^2, τ_s },

‘m6’ – { $S_f^2, \tau_f, S^2, \tau_s$ },

‘m7’ – { $S_f^2, S^2, \tau_s, R_{ex}$ },

‘m8’ – { $S_f^2, \tau_f, S^2, \tau_s, R_{ex}$ },

‘m9’ – {Rex}.

The preset model-free models with optimisation of the CSA value are

‘m10’ – {CSA},

‘m11’ – {CSA, S^2 },
 ‘m12’ – {CSA, S^2, τ_e },
 ‘m13’ – {CSA, S^2, R_{ex} },
 ‘m14’ – {CSA, S^2, τ_e, R_{ex} },
 ‘m15’ – {CSA, S_f^2, S^2, τ_s },

‘m16’ – {CSA, $S_f^2, \tau_f, S^2, \tau_s$ },
 ‘m17’ – {CSA, $S_f^2, S^2, \tau_s, R_{ex}$ },
 ‘m18’ – {CSA, $S_f^2, \tau_f, S^2, \tau_s, R_{ex}$ },
 ‘m19’ – {CSA, R_{ex} }.

The preset model-free models with optimisation of the bond length are

‘m20’ – {r},
 ‘m21’ – {r, S^2 },
 ‘m22’ – {r, S^2, τ_e },
 ‘m23’ – {r, S^2, R_{ex} },
 ‘m24’ – {r, S^2, τ_e, R_{ex} },
 ‘m25’ – {r, S_f^2, S^2, τ_s },
 ‘m26’ – {r, $S_f^2, \tau_f, S^2, \tau_s$ },
 ‘m27’ – {r, $S_f^2, S^2, \tau_s, R_{ex}$ },
 ‘m28’ – {r, $S_f^2, \tau_f, S^2, \tau_s, R_{ex}$ },
 ‘m29’ – {r, CSA, R_{ex} }.

The preset model-free models with both optimisation of the bond length and CSA are

‘m30’ – {r, CSA},
 ‘m31’ – {r, CSA, S^2 },
 ‘m32’ – {r, CSA, S^2, τ_e },
 ‘m33’ – {r, CSA, S^2, R_{ex} },
 ‘m34’ – {r, CSA, S^2, τ_e, R_{ex} },
 ‘m35’ – {r, CSA, S_f^2, S^2, τ_s },
 ‘m36’ – {r, CSA, $S_f^2, \tau_f, S^2, \tau_s$ },
 ‘m37’ – {r, CSA, $S_f^2, S^2, \tau_s, R_{ex}$ },
 ‘m38’ – {r, CSA, $S_f^2, \tau_f, S^2, \tau_s, R_{ex}$ },
 ‘m39’ – {r, CSA, R_{ex} }.

Warning: The models in the thirties range fail when using standard R_1 , R_2 , and NOE relaxation data. This is due to the extreme flexibility of these models where a change in the parameter ‘r’ is compensated by a corresponding change in the parameter ‘csa’ and vice versa.

The preset local tm models

Additional preset model-free models, which are simply extensions of the above models with the addition of a local τ_m parameter are:

'tm0' – $\{\tau_m\}$,
 'tm1' – $\{\tau_m, S^2\}$,
 'tm2' – $\{\tau_m, S^2, \tau_e\}$,
 'tm3' – $\{\tau_m, S^2, R_{ex}\}$,
 'tm4' – $\{\tau_m, S^2, \tau_e, R_{ex}\}$,
 'tm5' – $\{\tau_m, S_f^2, S^2, \tau_s\}$,
 'tm6' – $\{\tau_m, S_f^2, \tau_f, S^2, \tau_s\}$,
 'tm7' – $\{\tau_m, S_f^2, S^2, \tau_s, R_{ex}\}$,
 'tm8' – $\{\tau_m, S_f^2, \tau_f, S^2, \tau_s, R_{ex}\}$,
 'tm9' – $\{\tau_m, R_{ex}\}$.

The preset model-free models with optimisation of the CSA value are

'tm10' – $\{\tau_m, \text{CSA}\}$,
 'tm11' – $\{\tau_m, \text{CSA}, S^2\}$,
 'tm12' – $\{\tau_m, \text{CSA}, S^2, \tau_e\}$,
 'tm13' – $\{\tau_m, \text{CSA}, S^2, R_{ex}\}$,
 'tm14' – $\{\tau_m, \text{CSA}, S^2, \tau_e, R_{ex}\}$,
 'tm15' – $\{\tau_m, \text{CSA}, S_f^2, S^2, \tau_s\}$,
 'tm16' – $\{\tau_m, \text{CSA}, S_f^2, \tau_f, S^2, \tau_s\}$,
 'tm17' – $\{\tau_m, \text{CSA}, S_f^2, S^2, \tau_s, R_{ex}\}$,
 'tm18' – $\{\tau_m, \text{CSA}, S_f^2, \tau_f, S^2, \tau_s, R_{ex}\}$,
 'tm19' – $\{\tau_m, \text{CSA}, R_{ex}\}$.

The preset model-free models with optimisation of the bond length are

'tm20' – $\{\tau_m, r\}$,
 'tm21' – $\{\tau_m, r, S^2\}$,
 'tm22' – $\{\tau_m, r, S^2, \tau_e\}$,
 'tm23' – $\{\tau_m, r, S^2, R_{ex}\}$,
 'tm24' – $\{\tau_m, r, S^2, \tau_e, R_{ex}\}$,
 'tm25' – $\{\tau_m, r, S_f^2, S^2, \tau_s\}$,

'tm26' – $\{\tau_m, r, S_f^2, \tau_f, S^2, \tau_s\}$,

'tm27' – $\{\tau_m, r, S_f^2, S^2, \tau_s, R_{ex}\}$,

'tm28' – $\{\tau_m, r, S_f^2, \tau_f, S^2, \tau_s, R_{ex}\}$,

'tm29' – $\{\tau_m, r, \text{CSA}, R_{ex}\}$.

The preset model-free models with both optimisation of the bond length and CSA are

'tm30' – $\{\tau_m, r, \text{CSA}\}$,
 'tm31' – $\{\tau_m, r, \text{CSA}, S^2\}$,
 'tm32' – $\{\tau_m, r, \text{CSA}, S^2, \tau_e\}$,
 'tm33' – $\{\tau_m, r, \text{CSA}, S^2, R_{ex}\}$,
 'tm34' – $\{\tau_m, r, \text{CSA}, S^2, \tau_e, R_{ex}\}$,
 'tm35' – $\{\tau_m, r, \text{CSA}, S_f^2, S^2, \tau_s\}$,
 'tm36' – $\{\tau_m, r, \text{CSA}, S_f^2, \tau_f, S^2, \tau_s\}$,
 'tm37' – $\{\tau_m, r, \text{CSA}, S_f^2, S^2, \tau_s, R_{ex}\}$,
 'tm38' – $\{\tau_m, r, \text{CSA}, S_f^2, \tau_f, S^2, \tau_s, R_{ex}\}$,
 'tm39' – $\{\tau_m, r, \text{CSA}, R_{ex}\}$.

Spin identification string

If ‘spin_id’ is supplied then the model will only be selected for the corresponding spins. Otherwise the model will be selected for all spins.

Prompt examples

To pick model ‘m1’ for all selected spins, type:

```
relax> model_free.select_model('m1')
```

```
relax> model_free.select_model(model='m1')
```

Prompt examples

13.2.69 model_selection



Synopsis

Select the best model from a set of optimised models.

Defaults

```
model_selection(method='AIC', modsel_pipe=None,
bundle=None, pipes=None)
```

```
relax> model_selection('AIC', 'mixed')
relax> model_selection(method='AIC',
modsel_pipe='mixed')
relax> model_selection('AIC', 'mixed', ['m1',
'm2', 'm3', 'm4', 'm5'])
relax> model_selection(method='AIC',
modsel_pipe='mixed', pipes=['m1', 'm2',
'm3', 'm4', 'm5'])
```

Keyword arguments

method: The model selection technique (see below).

modsel_pipe: The name of the new data pipe which will be created by this user function by the copying of the selected data pipe.

bundle: The optional pipe bundle is a special grouping or clustering of data pipes. If this is specified, the newly created data pipe will be added to this bundle.

pipes: An array containing the names of all data pipes to include in model selection.

Description

The following model selection methods are supported:

AIC – Akaike's Information Criteria.

AICc – Small sample size corrected AIC.

BIC – Bayesian or Schwarz Information Criteria.

Bootstrap – Bootstrap model selection.

CV – Single-item-out cross-validation.

Expect – The expected overall discrepancy (the true values of the parameters are required).

Farrow – Old model-free method by Farrow et al., 1994.

Palmer – Old model-free method by Mandel et al., 1995.

Overall – The realised overall discrepancy (the true values of the parameters are required).

For the methods '**Bootstrap**', '**Expect**', and '**Overall**', the Monte Carlo simulations should have previously been executed with the `monte_carlo.create_data` method set to `Bootstrapping` to modify its behaviour.

If the data pipes have not been specified, then all data pipes will be used for model selection.

13.2.70 molecule.copy



Synopsis

Copy all data associated with a molecule.

Defaults

```
molecule.copy(pipe_from=None, mol_from=None,
pipe_to=None, mol_to=None)
```

Keyword arguments

pipe_from: The data pipe containing the molecule from which the data will be copied. This defaults to the current data pipe.

mol_from: The name of the molecule from which to copy data from.

pipe_to: The data pipe to copy the data to. This defaults to the current data pipe.

mol_to: The name of the new molecule. If left blank, the new molecule will have the same name as the old. This needs to be a molecule ID string, starting with '#'.

Description

This will copy all the data associated with a molecule to a second molecule. This includes all residue and spin system information. The new molecule name must be unique in the destination data pipe.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

Prompt examples

To copy the molecule data from the molecule 'GST' to the new molecule 'wt-GST', type:

```
relax> molecule.copy('#GST', '#wt-GST')
```

```
relax> molecule.copy(mol_from='#GST', mol_to
                      ='#wt-GST')
```

To copy the molecule data of the molecule 'Ap4Aase' from the data pipe 'm1' to 'm2', assuming the current data pipe is 'm1', type:

```
relax> molecule.copy(mol_from='#ApAase',
                      pipe_to='m2')
```

```
relax> molecule.copy(pipe_from='m1',
                      mol_from='#ApAase', pipe_to='m2',
                      mol_to='#ApAase')
```

13.2.71 molecule.create**Synopsis**

Create a new molecule.

Defaults

`molecule.create(mol_name=None, mol_type=None)`

Keyword arguments

`mol_name`: The name of the new molecule.

`mol_type`: The type of molecule.

Description

This adds a new molecule data container to the relax data storage object. The same molecule name cannot be used more than once. The molecule type need not be specified. However, if given, it should be one of ‘protein’, ‘DNA’, ‘RNA’, ‘organic molecule’, or ‘inorganic molecule’.

Prompt examples

To create the molecules ‘Ap4Aase’, ‘ATP’, and ‘MgF4’, type:

```
relax> molecule.create('Ap4Aase')
relax> molecule.create('ATP')
relax> molecule.create('MgF4')
```

13.2.72 molecule.delete**Synopsis**

Deleting molecules from the relax data store.

Defaults

`molecule.delete(mol_id=None)`

Keyword arguments

`mol_id`: The molecule ID string.

Description

This can be used to delete a single or sets of molecules from the relax data store. The molecule will be deleted from the current data pipe.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the ‘#’ character, the residue ID token beginning with the ‘:’ character, and the atom or spin system ID token beginning with the ‘@’ character. Each token can be composed of multiple elements - one per spin - separated by the ‘,’ character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the ‘-’ character. Negative numbers are supported. The full ID string specification is ‘#<mol_name> :<res_id>[, <res_id>, <res_id>, ...] @<atom_id>[, <atom_id>, <atom_id>, ...]’, where the token elements are ‘<mol_name>’, the name of the molecule, ‘<res_id>’, the residue identifier which can be a number, name, or range of numbers, ‘<atom_id>’, the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the ‘#’ character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string ‘@H*’ will select the protons ‘H’, ‘H2’, ‘H98’.

13.2.73 molecule.display



Synopsis

Display the molecule information.

Defaults

`molecule.display(mol_id=None)`

Keyword arguments

`mol_id`: The molecule ID string.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string 'CH*' will select the protons 'H', 'H2', 'H98'.

13.2.74 molecule.name



Synopsis

Name a molecule.

Defaults

`molecule.name(mol_id=None, name=None, force=False)`

Keyword arguments

`mol_id`: The molecule ID string corresponding to one or more molecules.

`name`: The new molecule name.

`force`: A flag which if True will cause the molecule to be renamed.

Description

This simply allows molecules to be named (or renamed).

Prompt examples

To rename the molecule 'Ap4Aase' to 'Inhib Ap4Aase', type one of:

```
relax> molecule.name('#Ap4Aase', 'Inhib
Ap4Aase', True)
```

```
relax> molecule.name(mol_id='#Ap4Aase', name
='Inhib Ap4Aase', force=True)
```

This assumes the molecule 'Ap4Aase' already exists.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

....] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.75 molecule.type



Synopsis

Set the molecule type.

Defaults

```
molecule.type(mol_id=None, type=None, force=False)
```

Keyword arguments

mol_id: The molecule ID string corresponding to one or more molecules.

type: The molecule type.

force: A flag which if True will cause the molecule type to be overwritten.

Description

This allows the type of the molecule to be specified. It can be one of:

```
'protein',
'DNA',
'RNA',
'organic molecule',
'inorganic molecule'.
```

Prompt examples

To set the molecule '#Ap4Aase' to the 'protein' type, type one of:

```
relax> molecule.type('#Ap4Aase', 'protein',
True)
```

```
relax> molecule.type(mol_id='#Ap4Aase', type
='protein', force=True)
```

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>, <res_id>, ...] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.76 molmol.clear_history

MOLMOL

Synopsis

Clear the Molmol command history.

Defaults

molmol.clear_history()

Description

This will clear the Molmol history from memory.

13.2.77 molmol.command**Synopsis**

```
Execute a user supplied Molmol command.
```

Defaults

molmol.command(command=None)

Keyword arguments

command: The Molmol command to execute.

Description

This allows Molmol commands to be passed to the program. This can be useful for automation or scripting.

Prompt examples

To reinitialise the Molmol instance, type:

```
relax> molmol.command("InitAll yes")
```

13.2.78 molmol.macro_apply**Synopsis**

```
Execute Molmol macros.
```

Defaults

molmol.macro_apply(data_type=None, style='classic', colour_start_name=None, colour_start_rgb=None, colour_end_name=None, colour_end_rgb=None, colour_list=None)

Keyword arguments

data_type: The data type to map to the structure.

style: The style of the macro.

colour_start_name: The name of the starting colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the starting colour RGB colour array cannot be given.

colour_start_rgb: The starting colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the starting colour name cannot be given.

colour_end_name: The name of the ending colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the ending colour RGB colour array cannot be given.

colour_end_rgb: The ending colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the ending colour name cannot be given.

colour_list: The colour list to search for the colour names. This can be either 'molmol' or 'x11'.

Description

This allows spin specific values to be mapped to a structure through Molmol macros. Currently only the 'classic' style, which is described below, is available.

Colour

The values are coloured based on a linear colour gradient which is specified through starting and ending colours. These can either be a string to identify one of the RGB (red, green, blue) colour arrays listed in the tables below, or you can give the RGB vector itself. For example, ‘white’ and [1.0, 1.0, 1.0] both select the same colour. Leaving both colours unset will select the default colour gradient which for each type of analysis is described below.

When supplying the colours as strings, two lists of colours can be selected from which to match the strings. These are the default Molmol colour list and the X11 colour list, both of which are described in the tables below. The default behaviour is to first search the Molmol list and then the X11 colour list, raising an error if neither contain the name. To explicitly select these lists, set the colour list to either ‘molmol’ or ‘x11’.

Model-free classic style

Creator: Edward d’Auvergne

Argument string: “classic”

Description: The classic style draws the backbone of a protein in a cylindrical bond style. Rather than colouring the amino acids to which the NH bond belongs, the three covalent bonds of the peptide bond from Ca to Ca in which the NH bond is located are coloured. Deselected residues are shown as black lines.

Supported data types:

Please see Table 13.18 on page 298.

Molmol RGB colour arrays

The following table is a list of colours used in Molmol and their corresponding RGB colour values ranging from 0 to 1.

Please see Table 13.19 on page 299.

X11 RGB colour arrays

The following table is the list of X11 colour names and their corresponding RGB colour values ranging from 0 to 255.

Please see Table 13.20 on page 300.

Table 13.18: The model-free classic style for mapping model spin specific data onto 3D molecular structures using either PyMOL or Molmol.

Data type	String	Description
S^2 .	's2'	The standard model-free order parameter, equal to $S_f^2 S_2$ s for the two timescale models. The default colour gradient starts at 'yellow' and ends at 'red'.
S_f^2 .	's2f'	The order parameter of the faster of two internal motions. Residues which are described by model-free models m1 to m4, the single timescale models, are illustrated as white neon bonds. The default colour gradient is the same as that for the S^2 data type.
S_s^2 .	's2s'	The order parameter of the slower of two internal motions. This functions exactly as S_f^2 except that S_s^2 is plotted instead.
Amplitude of fast motions.	'amp_fast'	Model independent display of the amplitude of fast motions. For residues described by model-free models m5 to m8, the value plotted is that of S_f^2 . However, for residues described by models m1 to m4, what is shown is dependent on the timescale of the motions. This is because these single timescale models can, at times, be perfect approximations to the more complex two timescale models. Hence if τ_e is less than 200 ps, S^2 is plotted. Otherwise the peptide bond is coloured white. The default colour gradient is the same as that for S^2 .
Amplitude of slow motions.	'amp_slow'	Model independent display of the amplitude of slow motions, arbitrarily defined as motions slower than 200 ps. For residues described by model-free models m5 to m8, the order parameter S^2 is plotted if $\tau_s > 200$ ps. For models m1 to m4, S^2 is plotted if $\tau_e > 200$ ps. The default colour gradient is the same as that for S^2 .
τ_e .	'te'	The correlation time, τ_e . The default colour gradient starts at 'turquoise' and ends at 'blue'.
τ_f .	'tf'	The correlation time, τ_f . The default colour gradient is the same as that of τ_e .
τ_s .	'ts'	The correlation time, τ_s . The default colour gradient starts at 'blue' and ends at 'black'.
Timescale of fast motions	'time_fast'	Model independent display of the timescale of fast motions. For models m5 to m8, only the parameter τ_f is plotted. For models m2 and m4, the parameter τ_e is plotted only if it is less than 200 ps. All other residues are assumed to have a correlation time of zero. The default colour gradient is the same as that of τ_e .
Timescale of slow motions	'time_slow'	Model independent display of the timescale of slow motions. For models m5 to m8, only the parameter τ_s is plotted. For models m2 and m4, the parameter τ_e is plotted only if it is greater than 200 ps. All other residues are coloured white. The default colour gradient is the same as that of τ_s .
Chemical exchange	'rex'	The chemical exchange, R_{ex} . Residues which experience no chemical exchange are coloured white. The default colour gradient starts at 'yellow' and finishes at 'red'.

Table 13.19: Molmol colour names and corresponding RGB colour values (from 0 to 1)

Name	Red	Green	Blue
'black'	0.000	0.000	0.000
'navy'	0.000	0.000	0.502
'blue'	0.000	0.000	1.000
'dark green'	0.000	0.392	0.000
'green'	0.000	1.000	0.000
'cyan'	0.000	1.000	1.000
'turquoise'	0.251	0.878	0.816
'royal blue'	0.255	0.412	0.882
'aquamarine'	0.498	1.000	0.831
'sky green'	0.529	0.808	0.922
'dark violet'	0.580	0.000	0.827
'pale green'	0.596	0.984	0.596
'purple'	0.627	0.125	0.941
'brown'	0.647	0.165	0.165
'light blue'	0.678	0.847	0.902
'grey'	0.745	0.745	0.745
'light grey'	0.827	0.827	0.827
'violet'	0.933	0.510	0.933
'light coral'	0.941	0.502	0.502
'khaki'	0.941	0.902	0.549
'beige'	0.961	0.961	0.863
'red'	1.000	0.000	0.000
'magenta'	1.000	0.000	1.000
'deep pink'	1.000	0.078	0.576
'orange red'	1.000	0.271	0.000
'hot pink'	1.000	0.412	0.706
'coral'	1.000	0.498	0.314
'dark orange'	1.000	0.549	0.000
'orange'	1.000	0.647	0.000
'pink'	1.000	0.753	0.796
'gold'	1.000	0.843	0.000
'yellow'	1.000	1.000	0.000
'light yellow'	1.000	1.000	0.878
'ivory'	1.000	1.000	0.941
'white'	1.000	1.000	1.000

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
snow	255	250	250
ghost white	248	248	255
white smoke	245	245	245
gainsboro	220	220	220
floral white	255	250	240
old lace	253	245	230
linen	250	240	230
antique white	250	235	215
papaya whip	255	239	213
blanched almond	255	235	205
bisque	255	228	196
peach puff	255	218	185
navajo white	255	222	173
moccasin	255	228	181
cornsilk	255	248	220
ivory	255	255	240
lemon chiffon	255	250	205
seashell	255	245	238
honeydew	240	255	240
mint cream	245	255	250
azure	240	255	255
alice blue	240	248	255
lavender	230	230	250
lavender blush	255	240	245
misty rose	255	228	225
white	255	255	255
black	0	0	0
dark slate grey	47	79	79
dim grey	105	105	105
slate grey	112	128	144
light slate grey	119	136	153
grey	190	190	190
light grey	211	211	211
midnight blue	25	25	112
navy	0	0	128
cornflower blue	100	149	237
dark slate blue	72	61	139
slate blue	106	90	205
medium slate blue	123	104	238
light slate blue	132	112	255
medium blue	0	0	205
royal blue	65	105	225
blue	0	0	255
dodger blue	30	144	255
deep sky blue	0	191	255
sky blue	135	206	235
light sky blue	135	206	250
steel blue	70	130	180
light steel blue	176	196	222
light blue	173	216	230
powder blue	176	224	230
pale turquoise	175	238	238
dark turquoise	0	206	209
medium turquoise	72	209	204
turquoise	64	224	208
cyan	0	255	255
light cyan	224	255	255
cadet blue	95	158	160
medium aquamarine	102	205	170
aquamarine	127	255	212
dark green	0	100	0
dark olive green	85	107	47
dark sea green	143	188	143
sea green	46	139	87
medium sea green	60	179	113
light sea green	32	178	170

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
pale green	152	251	152
spring green	0	255	127
lawn green	124	252	0
green	0	255	0
chartreuse	127	255	0
medium spring green	0	250	154
green yellow	173	255	47
lime green	50	205	50
yellow green	154	205	50
forest green	34	139	34
olive drab	107	142	35
dark khaki	189	183	107
khaki	240	230	140
pale goldenrod	238	232	170
light goldenrod yellow	250	250	210
light yellow	255	255	224
yellow	255	255	0
gold	255	215	0
light goldenrod	238	221	130
goldenrod	218	165	32
dark goldenrod	184	134	11
rosy brown	188	143	143
indian red	205	92	92
saddle brown	139	69	19
sienna	160	82	45
peru	205	133	63
burlywood	222	184	135
beige	245	245	220
wheat	245	222	179
sandy brown	244	164	96
tan	210	180	140
chocolate	210	105	30
firebrick	178	34	34
brown	165	42	42
dark salmon	233	150	122
salmon	250	128	114
light salmon	255	160	122
orange	255	165	0
dark orange	255	140	0
coral	255	127	80
light coral	240	128	128
tomato	255	99	71
orange red	255	69	0
red	255	0	0
hot pink	255	105	180
deep pink	255	20	147
pink	255	192	203
light pink	255	182	193
pale violet red	219	112	147
maroon	176	48	96
medium violet red	199	21	133
violet red	208	32	144
magenta	255	0	255
violet	238	130	238
plum	221	160	221
orchid	218	112	214
medium orchid	186	85	211
dark orchid	153	50	204
dark violet	148	0	211
blue violet	138	43	226
purple	160	32	240
medium purple	147	112	219
thistle	216	191	216
snow 1	255	250	250
snow 2	238	233	233
snow 3	205	201	201

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
snow 4	139	137	137
seashell 1	255	245	238
seashell 2	238	229	222
seashell 3	205	197	191
seashell 4	139	134	130
antique white 1	255	239	219
antique white 2	238	223	204
antique white 3	205	192	176
antique white 4	139	131	120
bisque 1	255	228	196
bisque 2	238	213	183
bisque 3	205	183	158
bisque 4	139	125	107
peach puff 1	255	218	185
peach puff 2	238	203	173
peach puff 3	205	175	149
peach puff 4	139	119	101
navajo white 1	255	222	173
navajo white 2	238	207	161
navajo white 3	205	179	139
navajo white 4	139	121	94
lemon chiffon 1	255	250	205
lemon chiffon 2	238	233	191
lemon chiffon 3	205	201	165
lemon chiffon 4	139	137	112
cornsilk 1	255	248	220
cornsilk 2	238	232	205
cornsilk 3	205	200	177
cornsilk 4	139	136	120
ivory 1	255	255	240
ivory 2	238	238	224
ivory 3	205	205	193
ivory 4	139	139	131
honeydew 1	240	255	240
honeydew 2	224	238	224
honeydew 3	193	205	193
honeydew 4	131	139	131
lavender blush 1	255	240	245
lavender blush 2	238	224	229
lavender blush 3	205	193	197
lavender blush 4	139	131	134
misty rose 1	255	228	225
misty rose 2	238	213	210
misty rose 3	205	183	181
misty rose 4	139	125	123
azure 1	240	255	255
azure 2	224	238	238
azure 3	193	205	205
azure 4	131	139	139
slate blue 1	131	111	255
slate blue 2	122	103	238
slate blue 3	105	89	205
slate blue 4	71	60	139
royal blue 1	72	118	255
royal blue 2	67	110	238
royal blue 3	58	95	205
royal blue 4	39	64	139
blue 1	0	0	255
blue 2	0	0	238
blue 3	0	0	205
blue 4	0	0	139
dodger blue 1	30	144	255
dodger blue 2	28	134	238
dodger blue 3	24	116	205
dodger blue 4	16	78	139
steel blue 1	99	184	255

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
steel blue 2	92	172	238
steel blue 3	79	148	205
steel blue 4	54	100	139
deep sky blue 1	0	191	255
deep sky blue 2	0	178	238
deep sky blue 3	0	154	205
deep sky blue 4	0	104	139
sky blue 1	135	206	255
sky blue 2	126	192	238
sky blue 3	108	166	205
sky blue 4	74	112	139
light sky blue 1	176	226	255
light sky blue 2	164	211	238
light sky blue 3	141	182	205
light sky blue 4	96	123	139
slate grey 1	198	226	255
slate grey 2	185	211	238
slate grey 3	159	182	205
slate grey 4	108	123	139
light steel blue 1	202	225	255
light steel blue 2	188	210	238
light steel blue 3	162	181	205
light steel blue 4	110	123	139
light blue 1	191	239	255
light blue 2	178	223	238
light blue 3	154	192	205
light blue 4	104	131	139
light cyan 1	224	255	255
light cyan 2	209	238	238
light cyan 3	180	205	205
light cyan 4	122	139	139
pale turquoise 1	187	255	255
pale turquoise 2	174	238	238
pale turquoise 3	150	205	205
pale turquoise 4	102	139	139
cadet blue 1	152	245	255
cadet blue 2	142	229	238
cadet blue 3	122	197	205
cadet blue 4	83	134	139
turquoise 1	0	245	255
turquoise 2	0	229	238
turquoise 3	0	197	205
turquoise 4	0	134	139
cyan 1	0	255	255
cyan 2	0	238	238
cyan 3	0	205	205
cyan 4	0	139	139
dark slate grey 1	151	255	255
dark slate grey 2	141	238	238
dark slate grey 3	121	205	205
dark slate grey 4	82	139	139
aquamarine 1	127	255	212
aquamarine 2	118	238	198
aquamarine 3	102	205	170
aquamarine 4	69	139	116
dark sea green 1	193	255	193
dark sea green 2	180	238	180
dark sea green 3	155	205	155
dark sea green 4	105	139	105
sea green 1	84	255	159
sea green 2	78	238	148
sea green 3	67	205	128
sea green 4	46	139	87
pale green 1	154	255	154
pale green 2	144	238	144
pale green 3	124	205	124

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
pale green 4	84	139	84
spring green 1	0	255	127
spring green 2	0	238	118
spring green 3	0	205	102
spring green 4	0	139	69
green 1	0	255	0
green 2	0	238	0
green 3	0	205	0
green 4	0	139	0
chartreuse 1	127	255	0
chartreuse 2	118	238	0
chartreuse 3	102	205	0
chartreuse 4	69	139	0
olive drab 1	192	255	62
olive drab 2	179	238	58
olive drab 3	154	205	50
olive drab 4	105	139	34
dark olive green 1	202	255	112
dark olive green 2	188	238	104
dark olive green 3	162	205	90
dark olive green 4	110	139	61
khaki 1	255	246	143
khaki 2	238	230	133
khaki 3	205	198	115
khaki 4	139	134	78
light goldenrod 1	255	236	139
light goldenrod 2	238	220	130
light goldenrod 3	205	190	112
light goldenrod 4	139	129	76
light yellow 1	255	255	224
light yellow 2	238	238	209
light yellow 3	205	205	180
light yellow 4	139	139	122
yellow 1	255	255	0
yellow 2	238	238	0
yellow 3	205	205	0
yellow 4	139	139	0
gold 1	255	215	0
gold 2	238	201	0
gold 3	205	173	0
gold 4	139	117	0
goldenrod 1	255	193	37
goldenrod 2	238	180	34
goldenrod 3	205	155	29
goldenrod 4	139	105	20
dark goldenrod 1	255	185	15
dark goldenrod 2	238	173	14
dark goldenrod 3	205	149	12
dark goldenrod 4	139	101	8
rosy brown 1	255	193	193
rosy brown 2	238	180	180
rosy brown 3	205	155	155
rosy brown 4	139	105	105
indian red 1	255	106	106
indian red 2	238	99	99
indian red 3	205	85	85
indian red 4	139	58	58
sienna 1	255	130	71
sienna 2	238	121	66
sienna 3	205	104	57
sienna 4	139	71	38
burlwood 1	255	211	155
burlwood 2	238	197	145
burlwood 3	205	170	125
burlwood 4	139	115	85
wheat 1	255	231	186

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
wheat 2	238	216	174
wheat 3	205	186	150
wheat 4	139	126	102
tan 1	255	165	79
tan 2	238	154	73
tan 3	205	133	63
tan 4	139	90	43
chocolate 1	255	127	36
chocolate 2	238	118	33
chocolate 3	205	102	29
chocolate 4	139	69	19
firebrick 1	255	48	48
firebrick 2	238	44	44
firebrick 3	205	38	38
firebrick 4	139	26	26
brown 1	255	64	64
brown 2	238	59	59
brown 3	205	51	51
brown 4	139	35	35
salmon 1	255	140	105
salmon 2	238	130	98
salmon 3	205	112	84
salmon 4	139	76	57
light salmon 1	255	160	122
light salmon 2	238	149	114
light salmon 3	205	129	98
light salmon 4	139	87	66
orange 1	255	165	0
orange 2	238	154	0
orange 3	205	133	0
orange 4	139	90	0
dark orange 1	255	127	0
dark orange 2	238	118	0
dark orange 3	205	102	0
dark orange 4	139	69	0
coral 1	255	114	86
coral 2	238	106	80
coral 3	205	91	69
coral 4	139	62	47
tomato 1	255	99	71
tomato 2	238	92	66
tomato 3	205	79	57
tomato 4	139	54	38
orange red 1	255	69	0
orange red 2	238	64	0
orange red 3	205	55	0
orange red 4	139	37	0
red 1	255	0	0
red 2	238	0	0
red 3	205	0	0
red 4	139	0	0
deep pink 1	255	20	147
deep pink 2	238	18	137
deep pink 3	205	16	118
deep pink 4	139	10	80
hot pink 1	255	110	180
hot pink 2	238	106	167
hot pink 3	205	96	144
hot pink 4	139	58	98
pink 1	255	181	197
pink 2	238	169	184
pink 3	205	145	158
pink 4	139	99	108
light pink 1	255	174	185
light pink 2	238	162	173
light pink 3	205	140	149

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
light pink 4	139	95	101
pale violet red 1	255	130	171
pale violet red 2	238	121	159
pale violet red 3	205	104	137
pale violet red 4	139	71	93
maroon 1	255	52	179
maroon 2	238	48	167
maroon 3	205	41	144
maroon 4	139	28	98
violet red 1	255	62	150
violet red 2	238	58	140
violet red 3	205	50	120
violet red 4	139	34	82
magenta 1	255	0	255
magenta 2	238	0	238
magenta 3	205	0	205
magenta 4	139	0	139
orchid 1	255	131	250
orchid 2	238	122	233
orchid 3	205	105	201
orchid 4	139	71	137
plum 1	255	187	255
plum 2	238	174	238
plum 3	205	150	205
plum 4	139	102	139
medium orchid 1	224	102	255
medium orchid 2	209	95	238
medium orchid 3	180	82	205
medium orchid 4	122	55	139
dark orchid 1	191	62	255
dark orchid 2	178	58	238
dark orchid 3	154	50	205
dark orchid 4	104	34	139
purple 1	155	48	255
purple 2	145	44	238
purple 3	125	38	205
purple 4	85	26	139
medium purple 1	171	130	255
medium purple 2	159	121	238
medium purple 3	137	104	205
medium purple 4	93	71	139
thistle 1	255	225	255
thistle 2	238	210	238
thistle 3	205	181	205
thistle 4	139	123	139
grey 0	0	0	0
grey 1	3	3	3
grey 2	5	5	5
grey 3	8	8	8
grey 4	10	10	10
grey 5	13	13	13
grey 6	15	15	15
grey 7	18	18	18
grey 8	20	20	20
grey 9	23	23	23
grey 10	26	26	26
grey 11	28	28	28
grey 12	31	31	31
grey 13	33	33	33
grey 14	36	36	36
grey 15	38	38	38
grey 16	41	41	41
grey 17	43	43	43
grey 18	46	46	46
grey 19	48	48	48
grey 20	51	51	51

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
grey 21	54	54	54
grey 22	56	56	56
grey 23	59	59	59
grey 24	61	61	61
grey 25	64	64	64
grey 26	66	66	66
grey 27	69	69	69
grey 28	71	71	71
grey 29	74	74	74
grey 30	77	77	77
grey 31	79	79	79
grey 32	82	82	82
grey 33	84	84	84
grey 34	87	87	87
grey 35	89	89	89
grey 36	92	92	92
grey 37	94	94	94
grey 38	97	97	97
grey 39	99	99	99
grey 40	102	102	102
grey 41	105	105	105
grey 42	107	107	107
grey 43	110	110	110
grey 44	112	112	112
grey 45	115	115	115
grey 46	117	117	117
grey 47	120	120	120
grey 48	122	122	122
grey 49	125	125	125
grey 50	127	127	127
grey 51	130	130	130
grey 52	133	133	133
grey 53	135	135	135
grey 54	138	138	138
grey 55	140	140	140
grey 56	143	143	143
grey 57	145	145	145
grey 58	148	148	148
grey 59	150	150	150
grey 60	153	153	153
grey 61	156	156	156
grey 62	158	158	158
grey 63	161	161	161
grey 64	163	163	163
grey 65	166	166	166
grey 66	168	168	168
grey 67	171	171	171
grey 68	173	173	173
grey 69	176	176	176
grey 70	179	179	179
grey 71	181	181	181
grey 72	184	184	184
grey 73	186	186	186
grey 74	189	189	189
grey 75	191	191	191
grey 76	194	194	194
grey 77	196	196	196
grey 78	199	199	199
grey 79	201	201	201
grey 80	204	204	204
grey 81	207	207	207
grey 82	209	209	209
grey 83	212	212	212
grey 84	214	214	214
grey 85	217	217	217
grey 86	219	219	219

Table 13.20: X11 colour names and corresponding RGB colour values

Name	Red	Green	Blue
grey 87	222	222	222
grey 88	224	224	224
grey 89	227	227	227
grey 90	229	229	229
grey 91	232	232	232
grey 92	235	235	235
grey 93	237	237	237
grey 94	240	240	240
grey 95	242	242	242
grey 96	245	245	245
grey 97	247	247	247
grey 98	250	250	250
grey 99	252	252	252
grey 100	255	255	255
dark grey	169	169	169
dark blue	0	0	139
dark cyan	0	139	139
dark magenta	139	0	139
dark red	139	0	0
light green	144	238	144

Prompt examples

To map the order parameter values, S^2 , onto the structure using the classic style, type:

```
relax> molmol.macro_apply('s2')
relax> molmol.macro_apply(data_type='s2')
relax> molmol.macro_apply(data_type='s2',
    style="classic")
```

13.2.79 molmol.macro_run



Synopsis

Open and execute the Molmol macro file.

Defaults

```
molmol.macro_run(file=None, dir='molmol')
```

Keyword arguments

file: The name of the Molmol macro file.

dir: The directory name.

Description

This user function is for opening and running a Molmol macro located within a text file.

Prompt examples

To execute the macro file ‘s2.mac’ located in the directory ‘molmol’, type:

```
relax> molmol.macro_run(file='s2.mac')
relax> molmol.macro_run(file='s2.mac', dir='molmol')
```

Colour

13.2.80 molmol.macro_write




Synopsis

Create Molmol macros.

Defaults

```
molmol.macro_write(data_type=None, style='classic',
colour_start_name=None, colour_start_rgb=None,
colour_end_name=None, colour_end_rgb=None,
colour_list=None, file=None, dir='molmol', force=False)
```

Keyword arguments

data_type: The data type to map to the structure.

style: The style of the macro.

colour_start_name: The name of the starting colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the starting colour RGB colour array cannot be given.

colour_start_rgb: The starting colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the starting colour name cannot be given.

colour_end_name: The name of the ending colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the ending colour RGB colour array cannot be given.

colour_end_rgb: The ending colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the ending colour name cannot be given.

colour_list: The colour list to search for the colour names. This can be either ‘molmol’ or ‘x11’.

file: The optional name of the file.

dir: The optional directory to save the file to.

force: A flag which, if set to True, will cause the file to be overwritten.

Description

This allows residues specific values to be mapped to a structure through the creation of a Molmol ‘*.mac’ macro which can be executed in Molmol by clicking on ‘File, Macro, Execute User...’. Currently only the ‘classic’ style, which is described below, is available.

The values are coloured based on a linear colour gradient which is specified through starting and ending colours. These can either be a string to identify one of the RGB (red, green, blue) colour arrays listed in the tables below, or you can give the RGB vector itself. For example, ‘white’ and [1.0, 1.0, 1.0] both select the same colour. Leaving both colours unset will select the default colour gradient which for each type of analysis is described below.

When supplying the colours as strings, two lists of colours can be selected from which to match the strings. These are the default Molmol colour list and the X11 colour list, both of which are described in the tables below. The default behaviour is to first search the Molmol list and then the X11 colour list, raising an error if neither contain the name. To explicitly select these lists, set the colour list to either ‘molmol’ or ‘x11’.

Model-free classic style

Creator: Edward d’Auvergne

Argument string: “classic”

Description: The classic style draws the backbone of a protein in a cylindrical bond style. Rather than colouring the amino acids to which the NH bond belongs, the three covalent bonds of the peptide bond from Ca to Ca in which the NH bond is located are coloured. Deselected residues are shown as black lines.

Supported data types:

Please see Table 13.18 on page 298.

Molmol RGB colour arrays

The following table is a list of colours used in Molmol and their corresponding RGB colour values ranging from 0 to 1.

Please see Table 13.19 on page 299.

X11 RGB colour arrays

The following table is the list of X11 colour names and their corresponding RGB colour values ranging from 0 to 255.

Please see Table 13.20 on page 300.

Prompt examples

To create a Molmol macro mapping the order parameter values, S^2 , onto the structure using the classic style:

```
relax> molmol.macro_write('s2')
```

```
relax> molmol.macro_write(data_type='s2')

relax> molmol.macro_write(data_type='s2',
    style="classic", file='s2.mac', dir=
        molmol')
```

13.2.81 molmol.ribbon

MOLMOL

Synopsis

Apply the Molmol ribbon style.

Defaults

molmol.ribbon()

Description

This applies the Molmol ribbon style which is equivalent to clicking on ‘ribbon’ in the Molmol side menu. To do this, the following commands are executed:

```
CalcAtom 'H'  
CalcAtom 'HN'  
CalcSecondary  
XMacStand ribbon.mac
```

Prompt examples

To apply the ribbon style to the PDB file loaded, type:

```
relax> molmol.ribbon()
```

Then only the atoms and bonds of the geometric object are selected and the ‘ball/stick’ style applied:

13.2.82 molmol.tensor_pdb

MOLMOL

Synopsis

Display the diffusion tensor PDB geometric object over the loaded PDB.

SelectAtom ‘0’

SelectBond ‘0’

SelectAtom ‘:TNS’

SelectBond ‘:TNS’

XMacStand ball_stick.mac

The appearance is finally touched up:

Defaults

molmol.tensor_pdb(file=None)

RadiusAtom 1

SelectAtom ‘:TNS@C*’

RadiusAtom 1.5

Keyword arguments

file: The name of the PDB file containing the tensor geometric object.

Description

In executing this user function, a PDB file must have previously been loaded , a geometric object or polygon representing the Brownian rotational diffusion tensor will be overlain with the loaded PDB file and displayed within Molmol. The PDB file containing the geometric object must be created using the complementary structure.create_diff_tensor_pdb user function.

To display the diffusion tensor, the multiple commands will be executed. To overlay the structure with the diffusion tensor, everything will be selected and reoriented and moved to their original PDB frame positions:

```
SelectAtom “
SelectBond “
SelectAngle “
SelectDist “
SelectPrim “
RotateInit
MoveInit
```

Next the tensor PDB file is read in, selected, and the covalent bonds of the PDB CONECT records calculated:

```
ReadPdb file
SelectMol ‘@file’
CalcBond 1 1 1
```

13.2.83 molmol.view



Synopsis

View the collection of molecules from the loaded PDB file.

Defaults

`molmol.view()`

Description

This will simply launch Molmol.

Prompt examples

```
relax> molmol.view()
```

13.2.84 monte_carlo.create_data



Synopsis

Create the Monte Carlo simulation data.

Defaults

`monte_carlo.create_data(method='back_calc')`

Keyword arguments

`method`: The simulation method.

Description

The method can either be set to back calculation (Monte Carlo) or direct (bootstrapping), the choice of which determines the simulation type. If the values or parameters are calculated rather than minimised, this option will have no effect. Errors should only be propagated via Monte Carlo simulations if errors have been measured.

For error analysis, the method should be set to back calculation which will result in proper Monte Carlo simulations. The data used for each simulation is back calculated from the minimised model parameters and is randomised using Gaussian noise where the standard deviation is from the original error set. When the method is set to back calculation, this function should only be called after the model is fully minimised.

The simulation type can be changed by setting the method to direct. This will result in bootstrapping simulations which cannot be used in error analysis (and which are no longer Monte Carlo simulations). However, these simulations are required for certain model selection techniques (see the documentation for the model selection user function for details), and can be used for other purposes. Rather than the data being back calculated from the fitted model parameters, the data is generated by taking the original data and randomising using Gaussian noise with the standard deviations set to the original error set.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.

- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.
- 5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).
- 6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.
- 7 – Failed simulations are removed using the techniques of model elimination.
- 8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)
      # Step 2.

relax> minimise('newton')
      # Step 2.

relax> monte_carlo.setup(number=500)
      # Step 3.

relax> monte_carlo.create_data(method='
      back_calc')          # Step 4.

relax> monte_carlo.initial_values()
      # Step 5.
```

```
relax> minimise('newton')
      # Step 6.
```

```
relax> eliminate()
      # Step 7.
```

```
relax> monte_carlo.error_analysis()
      # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()
      # Step 2.
```

```
relax> monte_carlo.setup(number=500)
      # Step 3.
```

```
relax> monte_carlo.create_data(method='
      back_calc')          # Step 4.
```

```
relax> calc()
      # Step 6.
```

```
relax> monte_carlo.error_analysis()
      # Step 8.
```

13.2.85 monte_carlo.error_analysis



Synopsis

Calculate parameter errors from the Monte Carlo simulations.

Defaults

`monte_carlo.error_analysis()`

Description

Parameter errors are calculated as the standard deviation of the distribution of parameter values. This function should never be used if parameter values are obtained by minimisation and the simulation data are generated using the method ‘direct’. The reason is because only true Monte Carlo simulations can give the true parameter errors.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.
- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.
- 5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).

6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.

7 – Failed simulations are removed using the techniques of model elimination.

8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)                                # Step 2.

relax> minimise('newton')                                # Step 2.

relax> monte_carlo.setup(number=500)                      # Step 3.

relax> monte_carlo.create_data(method='back_calc')        # Step 4.

relax> monte_carlo.initial_values()                      # Step 5.

relax> minimise('newton')                                # Step 6.

relax> eliminate()                                     # Step 7.

relax> monte_carlo.error_analysis()                      # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()                                         # Step 2.

relax> monte_carlo.setup(number=500)                      # Step 3.

relax> monte_carlo.create_data(method='back_calc')        # Step 4.

relax> calc()                                         # Step 6.

relax> monte_carlo.error_analysis()                      # Step 8.
```

13.2.86 monte_carlo.initial_values



Synopsis

Set the initial simulation parameter values.

Defaults

monte_carlo.initial_values()

Description

This only effects where minimisation occurs and can therefore be skipped if the values or parameters are calculated rather than minimised. However, if accidentally run in this case, the results will be unaffected. It should only be called after the model or run is fully minimised. Once called, the functions ‘grid_search’ and ‘minimise’ will only effect the simulations and not the model parameters.

The initial values of the parameters for each simulation is set to the minimised parameters of the model. A grid search can be undertaken for each simulation instead, although this is computationally expensive and unnecessary. The minimisation function should be executed for a second time after running this function.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.
- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.

5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).

- 6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.
- 7 – Failed simulations are removed using the techniques of model elimination.
- 8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)                                # Step 2.

relax> minimise('newton')                                 # Step 2.

relax> monte_carlo.setup(number=500)                      # Step 3.

relax> monte_carlo.create_data(method='back_calc')        # Step 4.

relax> monte_carlo.initial_values()                       # Step 5.

relax> minimise('newton')                                 # Step 6.

relax> eliminate()                                       # Step 7.

relax> monte_carlo.error_analysis()                      # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()                                           # Step 2.
```

```

relax> monte_carlo.setup(number=500)
      # Step 3.

relax> monte_carlo.create_data(method='
back_calc')           # Step 4.

relax> calc()
      # Step 6.

relax> monte_carlo.error_analysis()
      # Step 8.

```

13.2.87 monte_carlo.off



Synopsis

Turn the Monte Carlo simulations off.

Defaults

monte_carlo.off()

Description

This will turn off the Monte Carlo simulations so that subsequent optimisation will operate directly on the model parameters and not on the simulations.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.
- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.
- 5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).
- 6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.

-
- 7 – Failed simulations are removed using the techniques of model elimination.
 - 8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)
          # Step 2.

relax> minimise('newton')
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')
          # Step 4.

relax> monte_carlo.initial_values()
          # Step 5.

relax> minimise('newton')
          # Step 6.

relax> eliminate()
          # Step 7.

relax> monte_carlo.error_analysis()
          # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')
          # Step 4.

relax> calc()
          # Step 6.

relax> monte_carlo.error_analysis()
          # Step 8.
```

13.2.88 monte_carlo.on



Synopsis

Turn the Monte Carlo simulations on.

Defaults

monte_carlo.on()

Description

This will turn on the Monte Carlo simulations so that subsequent optimisation will operate on the simulations rather than on the real model parameters.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.
- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.
- 5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).
- 6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.

7 – Failed simulations are removed using the techniques of model elimination.

8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)
          # Step 2.

relax> minimise('newton')
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')      # Step 4.

relax> monte_carlo.initial_values()
          # Step 5.

relax> minimise('newton')
          # Step 6.

relax> eliminate()
          # Step 7.

relax> monte_carlo.error_analysis()
          # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')      # Step 4.

relax> calc()
          # Step 6.

relax> monte_carlo.error_analysis()
          # Step 8.
```

13.2.89 monte_carlo.setup



Synopsis

Set up the Monte Carlo simulations.

Defaults

monte_carlo.setup(number=500)

Keyword arguments

number: The number of Monte Carlo simulations.

Description

This must be called prior to any of the other Monte Carlo functions. The effect is that the number of simulations will be set and that simulations will be turned on.

Monte Carlo Simulation Overview

For proper error analysis using Monte Carlo simulations, a sequence of function calls is required for running the various simulation components. The steps necessary for implementing Monte Carlo simulations are:

- 1 – The measured data set together with the corresponding error set should be loaded into relax.
- 2 – Either minimisation is used to optimise the parameters of the chosen model, or a calculation is run.
- 3 – To initialise and turn on Monte Carlo simulations, the number of simulations, n , needs to be set.
- 4 – The simulation data needs to be created either by back calculation from the fully minimised model parameters from step 2 or by direct calculation when values are calculated rather than minimised. The error set is used to randomise each simulation data set by assuming Gaussian errors. This creates a synthetic data set for each Monte Carlo simulation.
- 5 – Prior to minimisation of the parameters of each simulation, initial parameter estimates are required. These are taken as the optimised model parameters. An alternative is to use a grid search for each simulation to generate initial estimates, however this is extremely computationally expensive. For the case where values are calculated rather than minimised, this step should be skipped (although the results will be unaffected if this is accidentally run).

- 6 – Each simulation requires minimisation or calculation. The same techniques as used in step 2, excluding the grid search when minimising, should be used for the simulations.
- 7 – Failed simulations are removed using the techniques of model elimination.
- 8 – The model parameter errors are calculated from the distribution of simulation parameters.

Monte Carlo simulations can be turned on or off using functions within this class. Once the function for setting up simulations has been called, simulations will be turned on. The effect of having simulations turned on is that the functions used for minimisation (grid search, minimise, etc) or calculation will only affect the simulation parameters and not the model parameters. By subsequently turning simulations off using the appropriate function, the functions used in minimisation will affect the model parameters and not the simulation parameters.

An example for model-free analysis using the prompt UI mode which includes only the functions required for implementing the above steps is:

```
relax> grid_search(inc=11)
          # Step 2.

relax> minimise('newton')
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')
          # Step 4.

relax> monte_carlo.initial_values()
          # Step 5.

relax> minimise('newton')
          # Step 6.

relax> eliminate()
          # Step 7.

relax> monte_carlo.error_analysis()
          # Step 8.
```

An example for reduced spectral density mapping is:

```
relax> calc()
          # Step 2.

relax> monte_carlo.setup(number=500)
          # Step 3.

relax> monte_carlo.create_data(method='back_calc')
          # Step 4.

relax> calc()
          # Step 6.

relax> monte_carlo.error_analysis()
          # Step 8.
```

13.2.90 n_state_model.CoM



Synopsis

The defunct centre of mass (CoM) analysis.

Defaults

```
n_state_model.CoM(pivot_point=[0.0, 0.0, 0.0], centre=None)
```

Keyword arguments

pivot_point: The pivot point of the motions between the two domains.

centre: Manually specify the CoM of the initial position prior to the N rotations to the positions of the N states. This is optional.

Description

WARNING: This analysis is now defunct!

This is used for analysing the domain motion information content of the N states from the N-state model. The states do not correspond to physical states, hence nothing can be extracted from the individual states. This analysis involves the calculation of the pivot to centre of mass (pivot-CoM) order parameter and subsequent cone of motions.

For the analysis, both the pivot point and centre of mass must be specified. The supplied pivot point must be a vector of floating point numbers of length 3. If the centre of mass is supplied, it must also be a vector of floating point numbers (of length 3). If the centre of mass is not supplied, then the CoM will be calculated from the selected parts of a previously loaded structure.

Prompt examples

To perform an analysis where the pivot is at the origin and the CoM is set to the N-terminal domain of a previously loaded PDB file (the C-terminal domain has been deselected), type:

```
relax> n_state_model.CoM()
```

To perform an analysis where the pivot is at the origin (because the real pivot has been shifted to this position) and the CoM is at the position [0, 0, 1], type one of:

```
relax> n_state_model.CoM(centre=[0, 0, 1])
```

```
relax> n_state_model.CoM(centre=[0.0, 0.0, 1
    .0])
```

```
relax> n_state_model.CoM(pivot_point=[0.0, 0
    .0, 0.0], centre=[0.0, 0.0, 1.0])
```

13.2.91 n_state_model.cone_pdb



Synopsis

Create a PDB file representing the cone models from the centre of mass (CoM) analysis.

Defaults

```
n_state_model.cone_pdb(cone_type=None, scale=1.0,
file='cone.pdb', dir=None, force=False)
```

Keyword arguments

cone_type: The type of cone model to represent.

scale: Value for scaling the pivot-CoM distance which the size of the cone defaults to.

file: The name of the PDB file.

dir: The directory where the file is located.

force: A flag which, if set to True, will overwrite the any pre-existing file.

Description

WARNING: This analysis is now defunct!

This creates a PDB file containing an artificial geometric structure to represent the various cone models. These models include:

‘diff in cone’

‘diff on cone’

The model can be selected by setting the cone type to one of these values. The cone is represented as an isotropic cone with its axis parallel to the average pivot-CoM vector, the vertex placed at the pivot point of the domain motions, and the length of the edge of the cone equal to the pivot-CoM distance multiplied by the scaling factor. The resultant PDB file can subsequently read into any molecular viewer.

There are four different types of residue within the PDB. The pivot point is represented as a single carbon atom of the residue ‘PIV’. The cone consists of numerous H atoms of the residue ‘CON’. The average pivot-CoM vector is presented as the residue ‘AVE’ with one carbon atom positioned at the pivot and the other at the head of the

vector (after scaling by the scaling factor). Finally, if Monte Carlo have been performed, there will be multiple ‘MCC’ residues representing the cone for each simulation, and multiple ‘MCA’ residues representing the varying average pivot-CoM vector for each simulation.

To create the diffusion in a cone PDB representation, a uniform distribution of vectors on a sphere is generated using spherical coordinates with the polar angle defined from the average pivot-CoM vector. By incrementing the polar angle using an arccos distribution, a radial array of vectors representing latitude are created while incrementing the azimuthal angle evenly creates the longitudinal vectors. These are all placed into the PDB file as H atoms and are all connected using PDB CONECT records. Each H atom is connected to its two neighbours on the both the longitude and latitude. This creates a geometric PDB object with longitudinal and latitudinal lines representing the filled cone.

13.2.92 n_state_model.elim_no_prob



Synopsis

Eliminate the structures or states with no probability.

Defaults

`n_state_model.elim_no_prob()`

Description

This will simply remove the structures from the N-state analysis which have an optimised probability of zero.

Prompt examples

Simply type:

`relax> n_state_model.elim_no_prob(N=8)`

13.2.93 n_state_model.number_of_states
**Synopsis**

Set the number of states in the N-state model.

Defaults

```
n_state_model.number_of_states(N=1)
```

Keyword arguments

N: The number of states.

Description

Prior to optimisation, the number of states in the N-state model can be specified. If the number of states is not set, then this parameter will be equal to the number of loaded structures - the ensemble size.

Prompt examples

To set up an 8-state model, type:

```
relax> n_state_model.number_of_states(N=8)
```

13.2.94 n_state_model.ref_domain
**Synopsis**

Set the reference domain for the ‘2-domain’ N-state model.

Defaults

```
n_state_model.ref_domain(ref=None)
```

Keyword arguments

ref: The domain which will act as the frame of reference. This is only valid for the ‘2-domain’ N-state model.

Description

Prior to optimisation of the ‘2-domain’ N-state model, which of the two domains will act as the frame of reference must be specified. The N-states will be rotations of the other domain, so to switch the frame of reference to the other domain simply transpose the rotation matrices.

Prompt examples

To set up a 5-state model with ‘C’ domain being the frame of reference, type:

```
relax> n_state_model.ref_domain(ref='C')
```

13.2.95 n_state_model.select_model



13.2.96 noe.read_restraints



Synopsis

Select the N-state model type and set up the model.

Defaults

```
n_state_model.select_model(model='population')
```

Keyword arguments

model: The name of the preset N-state model.

Description

Prior to optimisation, the N-state model type should be selected. The preset models are:

'population' – The N-state model whereby only populations are optimised. The structures loaded into relax are assumed to be fixed, *i.e.* the orientations are not optimised, or if two domains are present the Euler angles for each state are fixed. The parameters of the model include the weight or probability for each state and the alignment tensors - {p0, p1, ..., pN, Axx, Ayy, Axy, Axz, Ayz, ...}.

'fixed' – The N-state model whereby all motions are fixed and all populations are fixed to the set probabilities. The parameters of the model are simply the parameters of each alignment tensor {Axx, Ayy, Axy, Axz, Ayz, ...}.

'2-domain' – The N-state model for a system of two domains, where one domain experiences a reduced tensor.

Prompt examples

To analyse populations of states, type:

```
relax> n_state_model.select_model(model='populations')
```

Synopsis

Read NOESY or ROESY restraints from a file.

Defaults

```
noe.read_restraints(file=None, dir=None, proton1_col=None, proton2_col=None, lower_col=None, upper_col=None, sep=None)
```

Keyword arguments

file: The name of the file containing the restraint data.

dir: The directory where the file is located.

proton1_col: The column containing the first proton of the NOE or ROE cross peak.

proton2_col: The column containing the second proton of the NOE or ROE cross peak.

lower_col: The column containing the lower NOE bound.

upper_col: The column containing the upper NOE bound.

sep: The column separator (the default is white space).

Description

The format of the file will be automatically determined, for example Xplor formatted restraint files. A generically formatted file is also supported if it contains minimally four columns with the two proton names and the upper and lower bounds, as specified by the column numbers. The proton names need to be in the spin ID string format.

Prompt examples

To read the Xplor formatted restraint file 'NOE.xpl', type one of:

```
relax> noe.read_restraints('NOE.xpl')
```

```
relax> noe.read_restraints(file='NOE.xpl')
```

To read the generic formatted file 'noes', type one of:

```
relax> noe.read_restraints(file='NOE.xpl', proton1_col=0, proton2_col=1, lower_col=2, upper_col=3)
```

13.2.97 noe.spectrum_type**Synopsis**

Set the steady-state NOE spectrum type for pre-loaded peak intensities.

Defaults

```
noe.spectrum_type(spectrum_type=None, spectrum_id=None)
```

Keyword arguments

spectrum_type: The type of steady-state NOE spectrum, one of ‘ref’ for the reference spectrum or ‘sat’ for the saturated spectrum.

spectrum_id: The spectrum ID string.

Description

The spectrum type can be one of the following:

The steady-state NOE reference spectrum.

The steady-state NOE spectrum with proton saturation turned on.

Peak intensities should be loaded before this user function via the spectrum.read_intensities user function. The intensity values will then be associated with a spectrum ID string which can be used here.

13.2.98 palmer.create**Synopsis**

Create the Modelfree4 input files.

Defaults

```
palmer.create(dir=None, force=False, binary='modelfree4', diff_search='none', sims=0, sim_type='pred', trim=0, steps=20, constraints=True, heteronuc_type='15N', atom1='N', atom2='H', spin_id=None)
```

Keyword arguments

dir: The directory to place the files.

force: A flag which if set to True will cause the results file to be overwritten if it already exists.

binary: The name of the executable Modelfree program file.

diff_search: See the Modelfree4 manual for ‘diffusion_search’.

sims: The number of Monte Carlo simulations.

sim_type: See the Modelfree4 manual.

trim: See the Modelfree4 manual.

steps: See the Modelfree4 manual.

constraints: A flag specifying whether the parameters should be constrained. The default is to turn constraints on (constraints=True).

heteronuc_type: A three letter string describing the heteronucleus type, ie ‘15N’, ‘13C’, etc.

atom1: The symbol of the X heteronucleus in the PDB file.

atom2: The symbol of the H nucleus in the PDB file.

spin_id: The spin identification string.

Description

The following files are created

‘dir/mfin’

‘dir/mfdata’

```
'dir/mfpar'
'dir/mfmodel'
'dir/run.sh'
```

The file ‘`dir/run.sh`’ contains the single command,

```
'modelfree4 -i mfin -d mfdata -p mfpar -m
mfmodel -o mfout -e out',
```

which can be used to execute modelfree4.

If you would like to use a different Modelfree executable file, change the binary name to the appropriate file name. If the file is not located within the environment’s path, include the full path in front of the binary file name.

13.2.99 palmer.execute



Synopsis

Perform a model-free optimisation using Modelfree4.

Defaults

palmer.execute(`dir=None`, `force=False`, `binary='modelfree4'`)

Keyword arguments

dir: The directory to place the files.

force: A flag which if set to True will cause the results file to be overwritten if it already exists.

binary: The name of the executable Modelfree program file.

Description

Modelfree 4 will be executed as

```
$ modelfree4 -i mfin -d mfdata -p mfpar -m
mfmodel -o mfout -e out
```

If a PDB file is loaded and non-isotropic diffusion is selected, then the file name will be placed on the command line as ‘`-s pdb_file_name`’.

If you would like to use a different Modelfree executable file, change the binary name to the appropriate file name. If the file is not located within the environment’s path, include the full path in front of the binary file name.

13.2.100 palmer.extract**Synopsis**

Extract data from the Modelfree4 ‘`mfout`’ star formatted file.

Defaults

```
palmer.extract(dir=None)
```

Keyword arguments

`dir`: The directory where the file ‘`mfout`’ is found.

Description

The model-free results will be extracted from the Modelfree4 results file ‘`mfout`’ located in the given directory.

13.2.101 paramag.centre**Synopsis**

Specify which atom is the paramagnetic centre.

Defaults

```
paramag.centre(pos=None, atom_id=None, pipe=None, verbosity=1, fix=True, ave_pos=True, force=False)
```

Keyword arguments

`pos`: The atomic position of the paramagnetic centre.

`atom_id`: The atom ID string.

`pipe`: The data pipe containing the structures to extract the centre from.

`verbosity`: The amount of information to print out.

`fix`: A flag specifying if the paramagnetic centre should be fixed during optimisation.

`ave_pos`: A flag specifying if the position of the atom is to be averaged across all models.

`force`: A flag which if True will cause the current paramagnetic centre to be overwritten.

Description

This is required for specifying where the paramagnetic centre is located in the loaded structure file. If no structure number is given, then the average atom position will be calculated if multiple structures are loaded.

A different set of structures than those loaded into the current data pipe can also be used to determine the position, or its average. This can be achieved by loading the alternative structures into another data pipe, and then specifying that pipe.

If the average position flag is set to True, the average position from all models will be used as the position of the paramagnetic centre. If False, then the positions from all structures will be used. If multiple positions are used, then a fast paramagnetic centre motion will be assumed so that PCSs for a single tensor will be calculated for each position, and the PCS values linearly averaged.

Prompt examples

If the paramagnetic centre is the lanthanide Dysprosium which is labelled as \mathfrak{D}_y in a loaded PDB file, then type one of:

```
relax> paramag.centre('Dy')
```

```
relax> paramag.centre(atom_id='Dy')
```

If the carbon atom ‘C1’ of residue ‘4’ in the PDB file is to be used as the paramagnetic centre, then type:

```
relax> paramag.centre(':4@C1')
```

To state that the Dy³⁺ atomic position is [0.136, 12.543, 4.356], type one of:

```
relax> paramag.centre([0.136, 12.543, 4.356])
```

```
relax> paramag.centre(pos=[0.136, 12.543, 4.356])
```

To find an unknown paramagnetic centre, type:

```
relax> paramag.centre(fix=False)
```

13.2.102 pcs.back_calc



Synopsis

Back calculate the pseudo-contact shifts.

Defaults

```
pcs.back_calc(align_id=None)
```

Keyword arguments

align_id: The alignment ID string.

Description

This will back calculate the pseudo-contact shifts if the paramagnetic centre, temperature and magnetic field strength has been specified, an alignment tensor is present, and atomic positions have been loaded into the relax data store.

13.2.103 pcs.calc_q_factors
**Synopsis**

Calculate the PCS Q factor for the selected spins.

Defaults

```
pcs.calc_q_factors(spin_id=None)
```

Keyword arguments

spin_id: The spin ID string for restricting to subset of all selected spins.

Description

For this to work, the back-calculated PCS data must first be generated by the analysis specific code. Otherwise a warning will be given.

Prompt examples

To calculate the PCS Q factor for only the spins ‘@H26’, ‘@H27’, and ‘@H28’, type one of:

```
relax> pcs.calc_q_factors('@H26 & @H27 &
    @H28')

relax> pcs.calc_q_factors(spin_id='@H26 &
    @H27 & @H28')
```

13.2.104 pcs.copy
**Synopsis**

Copy PCS data from one data pipe to another.

Defaults

```
pcs.copy(pipe_from=None, pipe_to=None, align_id=None)
```

Keyword arguments

pipe_from: The name of the pipe to copy the PCS data from.

pipe_to: The name of the pipe to copy the PCS data to.

align_id: The alignment ID string.

Description

This function will copy PCS data from ‘`pipe_from`’ to ‘`pipe_to`’. If `align_id` is not given then all PCS data will be copied, otherwise only a specific data set will be.

Prompt examples

To copy all PCS data from pipe ‘m1’ to pipe ‘m9’, type one of:

```
relax> pcs.copy('m1', 'm9')

relax> pcs.copy(pipe_from='m1', pipe_to='m9'
    )

relax> pcs.copy('m1', 'm9', None)

relax> pcs.copy(pipe_from='m1', pipe_to='m9',
    , align_id=None)
```

To copy only the ‘Th’ PCS data from ‘m3’ to ‘m6’, type one of:

```
relax> pcs.copy('m3', 'm6', 'Th')

relax> pcs.copy(pipe_from='m3', pipe_to='m6',
    , align_id='Th')
```

13.2.105 pcs.corr_plot**Synopsis**

Generate a correlation plot of the measured vs. the back-calculated PCSs.

Defaults

```
pcs.corr_plot(format='grace', file='pcs_corr_plot.agr',
dir=None, force=False)
```

Keyword arguments

format: The format of the plot data.

file: The name of the Grace file to create.

dir: The directory name.

force: A flag which if True will cause the file to be overwritten.

Description

Two formats are currently supported. If format is set to ‘grace’, then a Grace plot file will be created. If the format is not set then a plain text list of the measured and back-calculated data will be created.

Prompt examples

To create a Grace plot of the data, type:

```
relax> pcs.corr_plot()
```

To create a plain text list of the measured and back-calculated data, type one of:

```
relax> pcs.corr_plot(None)
```

```
relax> pcs.corr_plot(format=None)
```

13.2.106 pcs.delete**Synopsis**

Delete the PCS data corresponding to the alignment ID.

Defaults

```
pcs.delete(align_id=None)
```

Keyword arguments

align_id: The alignment ID string of the data to delete.

Description

This will delete all PCS data associated with the alignment ID in the current data pipe.

Prompt examples

To delete the PCS data corresponding to align_id='PH_gel', type:

```
relax> pcs.delete('PH_gel')
```

13.2.107 pcs.display**Synopsis**

Display the PCS data corresponding to the alignment ID.

Defaults

```
pcs.display(align_id=None, bc=False)
```

Keyword arguments

align_id: The alignment ID string.

bc: A flag which if set will display the back-calculated rather than measured RDCs.

Description

This will display all of the PCS data associated with the alignment ID in the current data pipe.

Prompt examples

To display the ‘phage’ PCS data, type:

```
relax> pcs.display('phage')
```

13.2.108 pcs.read**Synopsis**

Read the PCS data from file.

Defaults

```
pcs.read(align_id=None, file=None, dir=None, spin_id_col=None, mol_name_col=None, res_num_col=None, res_name_col=None, spin_num_col=None, spin_name_col=None, data_col=None, error_col=None, sep=None, spin_id=None)
```

Keyword arguments

align_id: The alignment ID string.

file: The name of the file containing the PCS data.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

data_col: The PCS data column.

error_col: The experimental error column.

sep: The column separator (the default is white space).

spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

Description

This will read PCS data from a file and associate it with an alignment ID, either a new ID or a preexisting one with no PCS data.

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number and name, and spin number and name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID can be used to restrict the reading to certain spin types, for example only 15N spins when only residue information is in the file.

Prompt examples

The following commands will read the PCS data out of the file ‘Tb.txt’ where the columns are separated by the symbol ‘,’, and store the PCSs under the ID ‘Tb’.

```
relax> pcs.read('Tb', 'Tb.txt', sep=',')
```

To read the 15N and 1H PCSs from the file ‘Eu.txt’, where the 15N values are in the 4th column and the 1H in the 9th, type both the following:

```
relax> pcs.read('Tb', 'Tb.txt', spin_id='@N'
                  , res_num_col=1, data_col=4)
```

```
relax> pcs.read('Tb', 'Tb.txt', spin_id='@H'
                  , res_num_col=1, data_col=9)
```

13.2.109 pcs.set_errors



Synopsis

Set the errors for the PCSs.

Defaults

```
pcs.set_errors(align_id=None, spin_id=None, sd=0.1)
```

Keyword arguments

align_id: The optional alignment ID string.

spin_id: The optional spin ID string.

sd: The PCS standard deviation value in ppm.

Description

If the PCS errors have not already been read from a PCS data file or if they need to be changed, then the errors can be set via this user function.

13.2.110 pcs.structural_noise



Synopsis

Determine the PCS error due to structural noise via simulation.

Defaults

```
pcs.structural_noise(align_id=None, rmsd=0.2, sim_num=1000, file=None, dir=None, force=False)
```

Keyword arguments

align_id: The optional alignment ID string.

rmsd: The atomic position RMSD, in Å, to randomise the spin positions with for the simulations.

sim_num: The number of simulations, N, to perform to determine the structural noise component of the PCS errors.

file: The optional name of the Grace file to plot the structural errors verses the paramagnetic centre to spin distances.

dir: The directory name to place the Grace file into.

force: A flag which if True will cause the file to be overwritten.

Description

The analysis of the pseudo-contact shift is influenced by two significant sources of noise - that of the NMR experiment and structural noise from the 3D molecular structure used. The closer the spin to the paramagnetic centre, the greater the influence of structural noise. This distance dependence is governed by the equation:

$$\sigma_{\text{dist}} = \frac{\sqrt{3} * |\delta| * \text{RMSD}}{r},$$

where σ_{dist} is the distance component of the structural noise as a standard deviation, δ is the PCS value, RMSD is the atomic position root-mean-square deviation, and r is the paramagnetic centre to spin distance. When close to the paramagnetic centre, this error source

can exceed that of the NMR experiment. The equation for the angular component of the structural noise is more complicated. The PCS error is influenced by distance, angle in the alignment frame, and the magnetic susceptibility tensor.

For the simulation the following must already be set up in the current data pipe:

The position of the paramagnetic centre.

The alignment and magnetic susceptibility tensor.

The protocol for the simulation is as follows:

The lanthanide or paramagnetic centre position will be fixed. Its motion is assumed to be on the femto- to pico- and nanosecond timescales. Hence the motion is averaged over the evolution of the PCS and can be ignored.

The positions of the nuclear spins will be randomised N times. For each simulation a random unit vector will be generated. Then a random distance along the unit vector will be generated by sampling from a Gaussian distribution centered at zero, the original spin position, with a standard deviation set to the given RMSD. Both positive and negative displacements will be used.

The PCS for the randomised position will be back calculated.

The PCS standard deviation will be calculated from the N randomised PCS values.

The standard deviation will both be stored in the spin container data structure in the relax data store as well as being added to the already present PCS error (using variance addition). This will then be used in any optimisations involving the PCS.

If the alignment ID string is not supplied, the procedure will be applied to the PCS data from all alignments.

13.2.111 pcs.weight**Synopsis**

`Set optimisation weights on the PCS data.`

Defaults

`pcs.weight(align_id=None, spin_id=None, weight=1.0)`

Keyword arguments

- `align_id`: The alignment ID string.
- `spin_id`: The spin ID string.
- `weight`: The weighting value.

Description

This can be used to force the PCS to contribute more or less to the chi-squared optimisation statistic. The higher the value, the more importance the PCS will have.

13.2.112 pcs.write**Synopsis**

`Write the PCS data to file.`

Defaults

`pcs.write(align_id=None, file=None, dir=None, bc=False, force=False)`

Keyword arguments

- `align_id`: The alignment ID string.
- `file`: The name of the file.
- `dir`: The directory name.

`bc`: A flag which if set will write out the back-calculated rather than measured RDCs.

`force`: A flag which if True will cause the file to be overwritten.

Description

If no directory name is given, the file will be placed in the current working directory. The alignment ID is required for selecting which PCS data set will be written to file.

13.2.113 pipe.bundle

**Synopsis**

The grouping of data pipes into a bundle.

Defaults

`pipe.bundle(bundle=None, pipe=None)`

Keyword arguments

`bundle`: The pipe bundle is a special grouping or clustering of data pipes.

`pipe`: The name of the data pipe to add to the bundle.

Description

Data pipes can be grouped or clustered together through special structures known as pipe bundles. If the specified data pipe bundle does not currently exist, it will be created.

Prompt examples

To add the data pipes ‘test 1’, ‘test 2’, and ‘test 3’ to the bundle ‘first analysis’, type the following:

```
relax> pipe.bundle('first analysis 1', 'test 1')
```

```
relax> pipe.bundle('first analysis 1', 'test 2')
```

```
relax> pipe.bundle('first analysis 1', 'test 3')
```

13.2.114 pipe.change_type

**Synopsis**

Change the type of the current data pipe.

Defaults

`pipe.change_type(pipe_type=None)`

Keyword arguments

`pipe_type`: The type of data pipe.

Description

The data pipe type must be one of the following:

‘ct’ – Consistency testing.

‘frame_order’ – Frame Order theories.

‘jw’ – Reduced spectral density mapping.

‘hybrid’ – Special hybrid pipe.

‘mf’ – Model-free analysis.

‘N-state’ – N-state model or ensemble analysis.

‘noe’ – Steady state NOE calculation.

‘relax_fit’ – Relaxation curve fitting.

Prompt examples

To change the type of the current ‘frame_order’ data pipe to the N-state model, type one of:

```
relax> pipe.change_type('N-state')
```

```
relax> pipe.change_type(pipe_type='N-state')
```

13.2.115 pipe.copy



Synopsis

Copy a data pipe.

Defaults

```
pipe.copy(pipe_from=None, pipe_to=None, bundle_to=None)
```

Keyword arguments

pipe_from: The name of the source data pipe to copy the data from.

pipe_to: The name of the target data pipe to copy the data to.

bundle_to: If given, the new data pipe will be grouped into this bundle.

Description

This allows the contents of a data pipe to be copied. If the source data pipe is not set, the current data pipe will be assumed. The target data pipe must not yet exist.

The optional bundling allows the newly created data pipe to be placed into either a new or existing data pipe bundle. If not specified, then the copied data pipe will not be associated with a bundle.

Prompt examples

To copy the contents of the ‘m1’ data pipe to the ‘m2’ data pipe, type:

```
relax> pipe.copy('m1', 'm2')
```

```
relax> pipe.copy(pipe_from='m1', pipe_to='m2')
      )
```

If the current data pipe is ‘m1’, then the following command can be used:

```
relax> pipe.copy(pipe_to='m2')
```

13.2.116 pipe.create



Synopsis

Add a new data pipe to the relax data store.

Defaults

```
pipe.create(pipe_name=None, pipe_type=None, bundle=None)
```

Keyword arguments

pipe_name: The name of the data pipe.

pipe_type: The type of data pipe.

bundle: The optional pipe bundle is a special grouping or clustering of data pipes. If this is specified, the newly created data pipe will be added to this bundle.

Description

The data pipe name can be any string however the data pipe type can only be one of the following:

‘ct’ – Consistency testing,

‘frame_order’ – The Frame Order theories,

‘jw’ – Reduced spectral density mapping,

‘hybrid’ – A special hybrid pipe,

‘mf’ – Model-free analysis,

‘N-state’ – N-state model of domain motions,

‘noe’ – Steady state NOE calculation,

‘relax_fit’ – Relaxation curve fitting,

The pipe bundling concept is simply a way of grouping data pipes together. This is useful for a number of purposes:

The grouping or categorisation of data pipes, for example when multiple related analyses are performed.

In the auto-analyses, as all the data pipes that they spawn are bound together within the original bundle.

In the graphical user interface mode as analysis tabs are linked to specific pipe bundles.

Prompt examples

To set up a model-free analysis data pipe with the name 'm5', type:

```
relax> pipe.create('m5', 'mf')
```

13.2.117 pipe.current



Synopsis

Print the name of the current data pipe.

Defaults

```
pipe.current()
```

Prompt examples

To run the user function, type:

```
relax> pipe.current()
```

13.2.118 pipe.delete**Synopsis**

Delete a data pipe from the relax data store.

Defaults

`pipe.delete(pipe_name=None)`

Keyword arguments

`pipe_name`: The name of the data pipe to delete.

Description

This will permanently remove the data pipe and all of its contents from the relax data store. If the pipe name is not given, then all data pipes will be deleted.

13.2.119 pipe.display**Synopsis**

Print a list of all the data pipes.

Defaults

`pipe.display()`

Prompt examples

To run the user function, type:

`relax> pipe.display()`



13.2.120 pipe.hybridise

**Synopsis**

Create a hybrid data pipe by fusing a number of other data pipes.

Defaults

```
pipe.hybridise(hybrid=None, pipes=None)
```

Keyword arguments

hybrid: The name of the hybrid data pipe to create.

pipes: An array containing the names of all data pipes to hybridise.

Description

This user function can be used to construct hybrid models. An example of the use of a hybrid model could be if the protein consists of two independent domains. These two domains could be analysed separately, each having their own optimised diffusion tensors. The N-terminal domain data pipe could be called ‘`N_sphere`’ while the C-terminal domain could be called ‘`C_ellipsoid`’. These two data pipes could then be hybridised into a single data pipe. This hybrid data pipe can then be compared via model selection to a data pipe whereby the entire protein is assumed to have a single diffusion tensor.

The requirements for data pipes to be hybridised is that the molecules, sequences, and spin systems for all the data pipes is the same, and that no spin system is allowed to be selected in two or more data pipes. The selections must not overlap to allow for rigorous statistical comparisons.

Prompt examples

The two data pipes ‘`N_sphere`’ and ‘`C_ellipsoid`’ could be hybridised into a single data pipe called ‘`mixed model`’ by typing:

```
relax> pipe.hybridise('mixed model', [
    'N_sphere', 'C_ellipsoid'])
```

```
relax> pipe.hybridise(hybrid='mixed model',
    pipes=['N_sphere', 'C_ellipsoid'])
```

13.2.121 pipe.switch

**Synopsis**

Switch between the data pipes of the relax data store.

**Defaults**

```
pipe.switch(pipe_name=None)
```

Keyword arguments

pipe_name: The name of the data pipe.

Description

This will switch between the various data pipes within the relax data store.

Prompt examples

To switch to the ‘`ellipsoid`’ data pipe, type:

```
relax> pipe.switch('ellipsoid')
```

```
relax> pipe.switch(pipe_name='ellipsoid')
```

13.2.122 pymol.cartoon**Synopsis**

Apply the PyMOL cartoon style and colour by secondary structure.

Defaults

pymol.cartoon()

Description

This applies the PyMOL cartoon style which is equivalent to hiding everything and clicking on show cartoon. It also colours the cartoon with red helices, yellow strands, and green loops. The following commands are executed:

```
cmd.hide('everything', file)
cmd.show('cartoon', file)
util.cbss(file, 'red', 'yellow', 'green')
```

where file is the file name without the '.pdb' extension.

Prompt examples

To apply this user function, type:

relax> pymol.cartoon()

13.2.123 pymol.clear_history**Synopsis**

Clear the PyMOL command history.

Defaults

pymol.clear_history()

Description

This will clear the Pymol history from memory.

13.2.124 pymol.command**Synopsis**

```
pymol.command(command=None)
```

Keyword arguments

command: The PyMOL command to execute.

Description

This allows PyMOL commands to be passed to the program. This can be useful for automation or scripting.

Prompt examples

To reinitialise the PyMOL instance, type:

```
relax> pymol.command("reinitialise")
```

13.2.125 pymol.cone_pdb**Synopsis**

```
pymol.cone_pdb(file=None)
```

Keyword arguments

file: The name of the PDB file containing the cone geometric object.

Description

The PDB file containing the geometric object must be created using the complementary frame_order.cone_pdb or *n*_state_model.cone_pdb user functions.

The cone PDB file is read in using the command:

```
load file
```

The average Com-pivot point vector, the residue ‘AVE’ is displayed using the commands:

```
select resn AVE
```

```
show sticks, ‘sele’
```

```
color blue, ‘sele’
```

The cone object, the residue ‘CON’, is displayed using the commands:

```
select resn CON
```

```
hide (“sele”)
```

```
show sticks, ‘sele’
```

```
color white, ‘sele’
```

Colour

13.2.126 pymol.macro_apply



Synopsis

Execute PyMOL macros.

Defaults

```
pymol.macro_apply(data_type=None, style='classic',
colour_start_name=None, colour_start_rgb=None,
colour_end_name=None, colour_end_rgb=None,
colour_list=None)
```

Keyword arguments

data_type: The data type to map to the structure.

style: The style of the macro.

colour_start_name: The name of the starting colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the starting colour RGB colour array cannot be given.

colour_start_rgb: The starting colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the starting colour name cannot be given.

colour_end_name: The name of the ending colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the ending colour RGB colour array cannot be given.

colour_end_rgb: The ending colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the ending colour name cannot be given.

colour_list: The colour list to search for the colour names. This can be either ‘molmol’ or ‘x11’.

Description

This allows spin specific values to be mapped to a structure through PyMOL macros. Currently only the ‘classic’ style, which is described below, is available.

The values are coloured based on a linear colour gradient which is specified through starting and ending colours. These can either be a string to identify one of the RGB (red, green, blue) colour arrays listed in the tables below, or you can give the RGB vector itself. For example, ‘white’ and [1.0, 1.0, 1.0] both select the same colour. Leaving both colours unset will select the default colour gradient which for each type of analysis is described below.

When supplying the colours as strings, two lists of colours can be selected from which to match the strings. These are the default Molmol colour list and the X11 colour list, both of which are described in the tables below. The default behaviour is to first search the Molmol list and then the X11 colour list, raising an error if neither contain the name. To explicitly select these lists, set the colour list to either ‘molmol’ or ‘x11’.

Model-free classic style

Creator: Edward d’Auvergne

Argument string: “classic”

Description: The classic style draws the backbone of a protein in a cylindrical bond style. Rather than colouring the amino acids to which the NH bond belongs, the three covalent bonds of the peptide bond from Ca to Ca in which the NH bond is located are coloured. Deselected residues are shown as black lines.

Supported data types:

Please see Table 13.18 on page 298.

Molmol RGB colour arrays

The following table is a list of colours used in Molmol and their corresponding RGB colour values ranging from 0 to 1.

Please see Table 13.19 on page 299.

X11 RGB colour arrays

The following table is the list of X11 colour names and their corresponding RGB colour values ranging from 0 to 255.

Please see Table 13.20 on page 300.

Prompt examples

To map the order parameter values, S^2 , onto the structure using the classic style, type:

```
relax> pymol.macro_apply('s2')
```

```
relax> pymol.macro_apply(data_type='s2')  
relax> pymol.macro_apply(data_type='s2',  
    style="classic")
```

13.2.127 pymol.macro_run



Synopsis

Open and execute the PyMOL macro file.

Defaults

```
pymol.macro_run(file=None, dir='pymol')
```

Keyword arguments

file: The name of the PyMOL macro file.

dir: The directory name.

Description

This user function is for opening and running a PyMOL macro located within a text file.

Prompt examples

To execute the macro file ‘s2.pml’ located in the directory ‘pymol’, type:

```
relax> pymol.macro_run(file='s2.pml')
```

```
relax> pymol.macro_run(file='s2.pml', dir='pymol')
```

Colour

13.2.128 pymol.macro_write



Synopsis

Create PyMOL macros.

Defaults

```
pymol.macro_write(data_type=None, style='classic',
colour_start_name=None, colour_start_rgb=None,
colour_end_name=None, colour_end_rgb=None,
colour_list=None, file=None, dir='pymol', force=False)
```

Keyword arguments

data_type: The data type to map to the structure.

style: The style of the macro.

colour_start_name: The name of the starting colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the starting colour RGB colour array cannot be given.

colour_start_rgb: The starting colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the starting colour name cannot be given.

colour_end_name: The name of the ending colour of the linear colour gradient. This can be either one of the X11 or one of the Molmol colour names listed in the description. If this is set, then the ending colour RGB colour array cannot be given.

colour_end_rgb: The ending colour of the linear colour gradient. This is an RGB colour array with values ranging from 0 to 1. If this is set, then the ending colour name cannot be given.

colour_list: The colour list to search for the colour names. This can be either ‘molmol’ or ‘x11’.

file: The optional name of the file.

dir: The optional directory to save the file to.

force: A flag which, if set to True, will cause the file to be overwritten.

Description

This allows residues specific values to be mapped to a structure through the creation of a PyMOL macro which can be executed in PyMOL by clicking on ‘File, Macro, Execute User...’. Currently only the ‘classic’ style, which is described below, is available.

The values are coloured based on a linear colour gradient which is specified through starting and ending colours. These can either be a string to identify one of the RGB (red, green, blue) colour arrays listed in the tables below, or you can give the RGB vector itself. For example, ‘white’ and [1.0, 1.0, 1.0] both select the same colour. Leaving both colours unset will select the default colour gradient which for each type of analysis is described below.

When supplying the colours as strings, two lists of colours can be selected from which to match the strings. These are the default Molmol colour list and the X11 colour list, both of which are described in the tables below. The default behaviour is to first search the Molmol list and then the X11 colour list, raising an error if neither contain the name. To explicitly select these lists, set the colour list to either ‘molmol’ or ‘x11’.

Model-free classic style

Creator: Edward d’Auvergne

Argument string: “classic”

Description: The classic style draws the backbone of a protein in a cylindrical bond style. Rather than colouring the amino acids to which the NH bond belongs, the three covalent bonds of the peptide bond from Ca to Ca in which the NH bond is located are coloured. Deselected residues are shown as black lines.

Supported data types:

Please see Table 13.18 on page 298.

Molmol RGB colour arrays

The following table is a list of colours used in Molmol and their corresponding RGB colour values ranging from 0 to 1.

Please see Table 13.19 on page 299.

X11 RGB colour arrays

The following table is the list of X11 colour names and their corresponding RGB colour values ranging from 0 to 255.

Please see Table 13.20 on page 300.

Prompt examples

To create a PyMOL macro mapping the order parameter values, S^2 , onto the structure using the classic style:

```
relax> pymol.macro_write('s2')
```

```
relax> pymol.macro_write(data_type='s2')

relax> pymol.macro_write(data_type='s2',
    style="classic", file='s2.pml', dir=
    pymol')
```

13.2.129 pymol.tensor_pdb



Synopsis

Display the diffusion tensor PDB geometric object over the loaded PDB.

Defaults

```
pymol.tensor_pdb(file=None)
```

Keyword arguments

file: The name of the PDB file containing the tensor geometric object.

Description

In executing this user function, a PDB file must have previously been loaded into this data pipe a geometric object or polygon representing the Brownian rotational diffusion tensor will be overlaid with the loaded PDB file and displayed within PyMOL. The PDB file containing the geometric object must be created using the complementary structure.create_diff_tensor_pdb user function.

The tensor PDB file is read in using the command:

```
load file
```

The centre of mass residue ‘COM’ is displayed using the commands:

```
select resn COM
show dots, 'sele'
color blue, 'sele'
```

The axes of the diffusion tensor, the residue ‘AXS’, is displayed using the commands:

```
select resn AXS
hide ('sele')
show sticks, 'sele'
color cyan, 'sele'
```

label ‘**sele**’, name

The simulation axes, the residues ‘**SIM**’, are displayed using the commands:



select resn SIM

colour cyan, ‘**sele**’

Synopsis

Display the PDB file representation of the XH vector distribution.

Defaults

pymol.vector_dist(file='XH_dist.pdb')

Keyword arguments

file: The name of the PDB file containing the vector distribution.

Description

A PDB file of the macromolecule must have previously been loaded as the vector distribution will be overlaid with the macromolecule within PyMOL. The PDB file containing the vector distribution must be created using the complementary structure.create_vector_dist user function.

The vector distribution PDB file is read in using the command:

load file

13.2.131 pymol.view**Synopsis**

View the collection of molecules from the loaded PDB file.

Defaults

`pymol.view()`

Description

This will simply launch Pymol.

Prompt examples

`relax> pymol.view()`

13.2.132 rdc.back_calc**Synopsis**

Back calculate the residual dipolar couplings.

Defaults

`rdc.back_calc(align_id=None)`

Keyword arguments

`align_id`: The alignment ID string.

Description

This will back calculate the residual dipolar couplings (RDCs) if an alignment tensor is present and inter-dipole vectors have been loaded into the relax data store.

13.2.133 rdc.calc_q_factors



Synopsis

Calculate the RDC Q factor for the selected spins.

Defaults

```
rdc.calc_q_factors(spin_id=None)
```

Keyword arguments

`spin_id`: The spin ID string for restricting to subset of all selected spins.

Description

For this to work, the back-calculated RDC data must first be generated by the analysis specific code. Otherwise a warning will be given.

Prompt examples

To calculate the RDC Q factor for only the spins ‘@H26’, ‘@H27’, and ‘@H28’, type one of:

```
relax> rdc.calc_q_factors('@H26 & @H27 & @H28')
```

```
relax> rdc.calc_q_factors(spin_id='@H26 & @H27 & @H28')
```

13.2.134 rdc.copy



Synopsis

Copy RDC data from one data pipe to another.

Defaults

```
rdc.copy(pipe_from=None, pipe_to=None, align_id=None)
```

Keyword arguments

`pipe_from`: The name of the pipe to copy the RDC data from.

`pipe_to`: The name of the pipe to copy the RDC data to.

`align_id`: The alignment ID string.

Description

This function will copy RDC data from ‘`pipe_from`’ to ‘`pipe_to`’. If `align_id` is not given then all RDC data will be copied, otherwise only a specific data set will be.

Prompt examples

To copy all RDC data from pipe ‘m1’ to pipe ‘m9’, type one of:

```
relax> rdc.copy('m1', 'm9')
```

```
relax> rdc.copy(pipe_from='m1', pipe_to='m9')
```

```
relax> rdc.copy('m1', 'm9', None)
```

```
relax> rdc.copy(pipe_from='m1', pipe_to='m9', align_id=None)
```

To copy only the ‘Th’ RDC data from ‘m3’ to ‘m6’, type one of:

```
relax> rdc.copy('m3', 'm6', 'Th')
```

```
relax> rdc.copy(pipe_from='m3', pipe_to='m6', align_id='Th')
```

13.2.135 rdc.corr_plot
**Synopsis**

Generate a correlation plot of the measured vs. the back-calculated RDCs.

Defaults

```
rdc.corr_plot(format='grace', file='rdc_corr_plot.agr', dir=None, force=False)
```

Keyword arguments

format: The format of the plot data.

file: The name of the Grace file to create.

dir: The directory name.

force: A flag which if True will cause the file to be overwritten.

Description

Two formats are currently supported. If format is set to ‘grace’, then a Grace plot file will be created. If the format is not set then a plain text list of the measured and back-calculated data will be created.

Prompt examples

To create a Grace plot of the data, type:

```
relax> rdc.corr_plot()
```

To create a plain text list of the measured and back-calculated data, type one of:

```
relax> rdc.corr_plot(None)
```

```
relax> rdc.corr_plot(format=None)
```

13.2.136 rdc.delete
**Synopsis**

Delete the RDC data corresponding to the alignment ID.

Defaults

```
rdc.delete(align_id=None)
```

Keyword arguments

align_id: The alignment ID string of the data to delete.

Description

This will delete all RDC data associated with the alignment ID in the current data pipe.

Prompt examples

To delete the RDC data corresponding to align_id=‘PH_gel’, type:

```
relax> rdc.delete('PH_gel')
```

13.2.137 rdc.display**Synopsis**

Display the RDC data corresponding to the alignment ID.

Defaults

```
rdc.display(align_id=None, bc=False)
```

Keyword arguments

align_id: The alignment ID string.

bc: A flag which if set will display the back-calculated rather than measured RDCs.

Description

This will display all of the RDC data associated with the alignment ID in the current data pipe.

Prompt examples

To display the ‘phage’ RDC data, type:

```
relax> rdc.display('phage')
```

13.2.138 rdc.read**Synopsis**

Read the RDC data from file.

Defaults

```
rdc.read(align_id=None, file=None, dir=None, data_type='D', spin_id1_col=1, spin_id2_col=2, data_col=None, error_col=None, sep=None, neg_g_corr=False, absolute=False)
```

Keyword arguments

align_id: The alignment ID string.

file: The name of the file containing the RDC data.

dir: The directory where the file is located.

data_type: Specify if the RDC data is in the D or 2D format, or the T = J + D format.

spin_id1_col: The spin ID string column for the first spin.

spin_id2_col: The spin ID string column for the second spin.

data_col: The RDC data column.

error_col: The experimental error column.

sep: The column separator (the default is white space).

neg_g_corr: A flag which is used to correct for the negative gyromagnetic ratio of 15N. If set to True, all RDC values will be inverted prior to being stored in the relax data store.

absolute: A flag which indicates that the loaded RDCs are signless.

Description

This will read RDC data from a file and associate it with an alignment ID, either a new ID or a preexisting one with no RDC data.

The data type is used to specify how the RDC is defined. It can be set to a number of values:

‘D’ means that the splitting in the aligned sample was taken as J + D.

‘2D’ means that the splitting in the aligned sample was assumed to be $J + 2D$.

‘T’ means that the file contains $T = J + D$ values.

Internally, relax uses the D notation. Therefore if set to ‘2D’, the values will be doubled when read in. If the ‘T’ data type is specified, then J couplings must be present for this data to be of any use.

If the negative gyromagnetic ratio correction flag is set, a sign inversion will be applied to all RDC values to be loaded. This is sometimes needed for 15N if the data is not compensated for the negative gyromagnetic ratio.

The absolute RDCs flag is used for RDCs in which the sign is unknown. All absolute RDCs loaded will be converted to positive values.

Prompt examples

The following commands will read the RDC data out of the file ‘Tb.txt’ where the columns are separated by the symbol ‘,’, and store the RDCs under the ID ‘Tb’:

```
relax> rdc.read('Tb', 'Tb.txt', sep=',')
```

If the individual spin RDC errors are located in the file ‘rdc_err.txt’ in column number 5, then to read these values into relax, assuming $J + D$ was measured, type one of:

```
relax> rdc.read('phage', 'rdc_err.txt',
    data_type='D', error_col=5)
```

```
relax> rdc.read(align_id='phage', file='
    rdc_err.txt', data_type='D', error_col
    =5)
```

13.2.139 rdc.set_errors



Synopsis

Set the errors for the RDCs.

Defaults

```
rdc.set_errors(align_id=None, spin_id1=None, spin_id2=
None, sd=1.0)
```

Keyword arguments

`align_id`: The optional alignment ID string.

`spin_id1`: The optional spin ID string of the first spin.

`spin_id2`: The optional spin ID string of the second spin.

`sd`: The RDC standard deviation value in Hertz.

Description

If the RDC errors have not already been read from a RDC data file or if they need to be changed, then the errors can be set via this user function.

13.2.140 rdc.weight**Synopsis**

Set optimisation weights on the RDC data.

Defaults

```
rdc.weight(align_id=None, spin_id=None, weight=1.0)
```

Keyword arguments

align_id: The alignment ID string.
spin_id: The spin ID string.
weight: The weighting value.

Description

This can be used to force the RDC to contribute more or less to the chi-squared optimisation statistic. The higher the value, the more importance the RDC will have.

13.2.141 rdc.write**Synopsis**

Write the RDC data to file.

Defaults

```
rdc.write(align_id=None, file=None, dir=None, bc=False, force=False)
```

Keyword arguments

align_id: The alignment ID string.
file: The name of the file.
dir: The directory name.
bc: A flag which if set will write out the back-calculated rather than measured RDCs.
force: A flag which if True will cause the file to be overwritten.

Description

If no directory name is given, the file will be placed in the current working directory. The alignment ID is required for selecting which RDC data set will be written to file.

13.2.142 relax_data.back_calc
**Synopsis**

Back calculate the relaxation data at the given frequency.

Defaults

```
relax_data.back_calc(ri_id=None, ri_type=None, frq=None)
```

Keyword arguments

ri_id: The relaxation data ID string.

ri_type: The relaxation data type, ie ‘R1’, ‘R2’, or ‘NOE’.

frq: The spectrometer frequency in Hz.

Description

This allows relaxation data of the given type and frequency to be back calculated from the model parameter values. If the relaxation data ID, type and frequency are not given, then relaxation data matching that currently loaded in the relax data store will be back-calculated.

13.2.143 relax_data.copy
**Synopsis**

Copy relaxation data from one pipe to another.

Defaults

```
relax_data.copy(pipe_from=None, pipe_to=None, ri_id=None)
```

Keyword arguments

pipe_from: The name of the pipe to copy the relaxation data from.

pipe_to: The name of the pipe to copy the relaxation data to.

ri_id: The relaxation data ID string.

Description

This will copy relaxation data from one data pipe to another. If the relaxation ID data string is not given then all relaxation data will be copied, otherwise only a specific data set will be copied.

Prompt examples

To copy all relaxation data from pipe ‘m1’ to pipe ‘m9’, type one of:

```
relax> relax_data.copy('m1', 'm9')

relax> relax_data.copy(pipe_from='m1',
                       pipe_to='m9')

relax> relax_data.copy('m1', 'm9', None)

relax> relax_data.copy(pipe_from='m1',
                       pipe_to='m9', ri_id=None)
```

To copy only the NOE relaxation data with the ID string of ‘NOE_800’ from ‘m3’ to ‘m6’, type one of:

```
relax> relax_data.copy('m3', 'm6', 'NOE_800'
                       )

relax> relax_data.copy(pipe_from='m3',
                       pipe_to='m6', ri_id='NOE_800')
```

13.2.144 relax_data.delete**Synopsis**

Delete the data corresponding to the relaxation data ID string.

Defaults

```
relax_data.delete(ri_id=None)
```

Keyword arguments

`ri_id`: The relaxation data ID string.

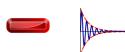
Description

The relaxation data corresponding to the given relaxation data ID string will be removed from the current data pipe.

Prompt examples

To delete the relaxation data corresponding to the ID ‘NOE_600’, type:

```
relax> relax_data.delete('NOE_600')
```

13.2.145 relax_data.display**Synopsis**

Display the data corresponding to the relaxation data ID string.

Defaults

```
relax_data.display(ri_id=None)
```

Keyword arguments

`ri_id`: The relaxation data ID string.

Description

This will display the relaxation data corresponding to the given ID.

Prompt examples

To display the NOE relaxation data at 600 MHz with the ID string ‘NOE_600’, type:

```
relax> relax_data.display('NOE_600')
```

13.2.146 relax_data.peak_intensity_type



Synopsis

Specify if heights or volumes were used to measure the peak intensities.

Defaults

```
relax_data.peak_intensity_type(ri_id=None, type='height')
```

Keyword arguments

ri_id: The relaxation data ID string.

type: The peak intensity type.

Description

This is essential for BMRB data deposition. It is used to specify whether peak heights or peak volumes were measured. The two currently allowed values for the peak intensity type are ‘height’ and ‘volume’.

13.2.147 relax_data.read



Synopsis

Read R₁, R₂, or NOE relaxation data from a file.

Defaults

```
relax_data.read(ri_id=None, ri_type=None, frq=None,
file=None, dir=None, spin_id_col=None, mol_name_col=
None, res_num_col=None, res_name_col=None,
spin_num_col=None, spin_name_col=None, data_col=
None, error_col=None, sep=None, spin_id=None)
```

Keyword arguments

ri_id: The relaxation data ID string. This must be a unique identifier.

ri_type: The relaxation data type, i.e. ‘R1’, ‘R2’, or ‘NOE’.

frq: The exact proton frequency of the spectrometer in Hertz. See the ‘sfrq’ parameter in the Varian procpqr file or the ‘SF01’ parameter in the Bruker acqus file.

file: The name of the file containing the relaxation data.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

data_col: The relaxation data column.

error_col: The experimental error column.

sep: The column separator (the default is white space).

spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

Description

This will load the relaxation data into the relax data store. The data is associated with the spectrometer frequency in Hertz. For subsequent analysis, this frequency must be set to the exact field strength. This value is stored in the ‘`sfrq`’ parameter in the Varian procpar file or the ‘`SF01`’ parameter in the Bruker acqus file.

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number, residue name, spin number and/or spin name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID string can be used to restrict the reading to certain spin types, for example only ¹⁵N spins when only residue information is in the file.

Prompt examples

The following commands will read the protein NOE relaxation data collected at 600 MHz out of a file called ‘`noe.600.out`’ where the residue numbers, residue names, data, errors are in the first, second, third, and forth columns respectively.

```
relax> relax_data.read('NOE_600', 'NOE', 599
    .7 * 1e6, 'noe.600.out', res_num_col=1,
    res_name_col=2, data_col=3, error_col
    =4)
```

```
relax> relax_data.read(ri_id='NOE_600',
    ri_type='NOE', frq=600.0 * 1e6, file='
    noe.600.out', res_num_col=1,
    res_name_col=2, data_col=3, error_col
    =4)
```

The following commands will read the R₂ data out of the file ‘`r2.out`’ where the residue numbers, residue names, data, errors are in the second, third, fifth, and sixth columns respectively. The columns are separated by commas.

```
relax> relax_data.read('R2_800', 'R2', 8.0 *
    1e8, 'r2.out', res_num_col=2,
    res_name_col=3, data_col=5, error_col
    =6, sep=',')
```

```
relax> relax_data.read(ri_id='R2_800',
    ri_type='R2', frq=8.0*1e8, file='r2.out
    ', res_num_col=2, res_name_col=3,
    data_col=5, error_col=6, sep=',')
```

The following commands will read the R₁ data out of the file ‘`r1.out`’ where the columns are separated by the symbol ‘%’

```
relax> relax_data.read('R1_300', 'R1', 300.1
    * 1e6, 'r1.out', sep='%')
```

13.2.148 relax_data.temp_calibration



Synopsis

Specify the per-experiment temperature calibration method used.

Defaults

```
relax_data.temp_calibration(ri_id=None, method=None)
```

Keyword arguments

`ri_id`: The relaxation data ID string.

`method`: The per-experiment temperature calibration method.

Description

For the proper measurement of relaxation data, per-experiment temperature calibration is essential. This user function is not for inputting standard MeOH/ethylene glycol/etc. calibration of a spectrometer - this temperature setting is of no use when you are running experiments which pump in large amounts of power into the probe head.

The R₁ experiment should be about the same temperature as a HSQC and hence be close to the standard MeOH/ethylene glycol spectrometer calibration. However the R₂ CPMG or spin lock and, to a lesser extent, the NOE pre-saturation pump a lot more power into the probe head. The power differences can either cause the temperature in the sample to be too high or too low. This is unpredictable as the thermometer used by the VT unit is next to the coils in the probe head and not inside the NMR sample. So the VT unit tries to control the temperature inside the probe head rather than in the NMR sample. However between the thermometer and the sample is the water of the sample, the glass of the NMR tube, the air gap where the VT unit controls air flow and the outside components of the probe head protecting the electronics. If the sample, the probe head or the VT unit is changed, this will have a different affect on the per-experiment temperature. The VT unit responds differently under different conditions and may sometimes over or under compensate by a couple of degrees. Therefore each relaxation data set from each spectrometer requires a per-experiment calibration.

Specifying the per-experiment calibration method is needed for BMRB data deposition. The currently allowed methods are:

```
'methanol',
'monoethylene glycol',
'no calibration applied'.
```

Other methods will be accepted if supplied.

13.2.149 relax_data.temp_control



Synopsis

Specify the temperature control method used.

Defaults

```
relax_data.temp.control(ri_id=None, method=None)
```

Keyword arguments

`ri_id`: The relaxation data ID string.

`method`: The control method.

Description

For the proper measurement of relaxation data, explicit temperature control techniques are essential. A number of factors can cause significant temperature fluctuations between individual relaxation experiments. This includes the daily temperature cycle of the room housing the spectrometer, different amounts of power for the individual experiments, etc.

The best methods for eliminating such problems are single scan interleaving and temperature compensation block. Single scan interleaving is the most powerful technique for averaging the temperature fluctuations not only across different experiments, but also across the entire measurement time. The application of off-resonance temperature compensation blocks at the start of the experiment is useful for the R_2 and will normalise the temperature between the individual experiments, but single scan or single fid interleaving is nevertheless required for normalising the temperature across the entire measurement.

Specifying the temperature control method is needed for BMRB data deposition. The currently allowed methods are:

```
'single scan interleaving',
'temperature compensation block',
'single scan interleaving and temperature
compensation block',
'single fid interleaving',
'single experiment interleaving',
'no temperature control applied'.
```

13.2.150 relax_data.type**Synopsis**

Set the type of relaxation data.

Defaults

```
relax_data.type(ri_id=None, ri_type=None)
```

Keyword arguments

ri_id: The relaxation data ID string of the data to set the frequency of.

ri_type: The relaxation data type, *i.e.* ‘R1’, ‘R2’, or ‘NOE’.

Description

This allows the type associated with the relaxation data to be either set or reset. This type must be one of ‘R1’, ‘R2’, or ‘NOE’.

13.2.151 relax_data.write**Synopsis**

Write relaxation data to a file.

Defaults

```
relax_data.write(ri_id=None, file=None, dir=None, bc=False, force=False)
```

Keyword arguments

ri_id: The relaxation data ID string.

file: The name of the file.

dir: The directory name.

bc: A flag which if True will cause the back-calculated data to be written to the file.

force: A flag which if True will cause the file to be overwritten.

Description

If no directory name is given, the file will be placed in the current working directory. The relaxation data ID string is required for selecting which relaxation data to write to file.

13.2.152 relax_fit.relax_time**Synopsis**

Set the relaxation delay time associated with each spectrum.

Defaults

```
relax_fit.relax_time(time=0.0, spectrum_id=None)
```

Keyword arguments

time: The time, in seconds, of the relaxation period.

spectrum_id: The spectrum identification string.

Description

Peak intensities should be loaded before calling this user function via the `spectrum.read_intensities` user function. The intensity values will then be associated with a spectrum identifier. To associate each spectrum identifier with a time point in the relaxation curve prior to optimisation, this user function should be called.

13.2.153 relax_fit.select_model**Synopsis**

Select the relaxation curve type.

Defaults

```
relax_fit.select_model(model='exp')
```

Keyword arguments

model: The type of relaxation curve to fit.

Description

The supported relaxation experiments include the default two parameter exponential fit, selected by setting the model type to ‘exp’, and the three parameter inversion recovery experiment in which the peak intensity limit is a non-zero value, selected by setting the model to ‘inv’.

The parameters of these two models are

‘exp’ – [Rx, I0],

‘inv’ – [Rx, I0, Iinf].



13.2.154 reset**Synopsis**

Reinitialise the relax data storage object.

Defaults

`reset()`

Description

All of the data of the relax data storage object will be erased and hence relax will return to its initial state.

13.2.155 residue.copy**Synopsis**

Copy all data associated with a residue.

Defaults

`residue.copy(pipe_from=None, res_from=None, pipe_to=None, res_to=None)`

Keyword arguments

`pipe_from`: The data pipe containing the residue from which the data will be copied. This defaults to the current data pipe.

`res_from`: The residue ID string of the residue to copy the data from.

`pipe_to`: The data pipe to copy the data to. This defaults to the current data pipe.

`res_to`: The residue ID string of the residue to copy the data to. If left blank, the new residue will have the same name as the old.

Description

This will copy all the data associated with the identified residue to the new, non-existent residue. The new residue cannot currently exist.

Prompt examples

To copy the residue data from residue 1 to the new residue 2, type:

```
relax> residue.copy(res_from=':1', res_to=':2')
```

To copy residue 1 of the molecule ‘Old mol’ to residue 5 of the molecule ‘New mol’, type:

```
relax> residue.copy(res_from='#Old mol:1',
                      res_to='#New mol:5')
```

To copy the residue data of residue 1 from the data pipe ‘m1’ to ‘m2’, assuming the current data pipe is ‘m1’, type:

```
relax> residue.copy(res_from=':1', pipe_to='m2')
```

```
relax> residue.copy(pipe_from='m1', res_from=':1',
                      pipe_to='m2', res_to=':1')
```

13.2.156 residue.create



Synopsis

Create a new residue.

Defaults

```
residue.create(res_num=None, res_name=None,
mol_name=None)
```

Keyword arguments

`res_num`: The residue number.

`res_name`: The name of the residue.

`mol_name`: The name of the molecule to add the residue to.

Description

Using this, a new sequence can be generated without using the sequence user functions. However if the sequence already exists, the new residue will be added to the end of the residue list (the residue numbers of this list need not be sequential). The same residue number cannot be used more than once. A corresponding single spin system will be created for this residue. The spin system number and name or additional spin systems can be added later if desired.

Prompt examples

The following sequence of commands will generate the sequence 1 ALA, 2 GLY, 3 LYS:

```
relax> residue.create(1, 'ALA')
relax> residue.create(2, 'GLY')
relax> residue.create(3, 'LYS')
```

13.2.157 residue.delete



Synopsis

Delete residues from the current data pipe.

Defaults

```
residue.delete(res_id=None)
```

Keyword arguments

`res_id`: The residue ID string.

Description

This can be used to delete a single or sets of residues. See the ID string documentation for more information. If spin system/atom ids are included a RelaxError will be raised.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.158 residue.display**Synopsis**

Display information about the residue(s).

Defaults

`residue.display(res_id=None)`

Keyword arguments

`res_id`: The residue ID string.

Description

This will display the residue data loaded into the current data pipe.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.159 residue.name**Synopsis**

Name the residues.

Defaults

`residue.name(res_id=None, name=None, force=False)`

Keyword arguments

`res_id`: The residue ID string corresponding to one or more residues.

`name`: The new name.

`force`: A flag which if True will cause the residue to be renamed.

Description

This simply allows residues to be named (or renamed).

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

Prompt examples

The following sequence of commands will rename the sequence {1 ALA, 2 GLY, 3 LYS} to {1 XXX, 2 XXX, 3 XXX}:

```
relax> residue.name(':1', 'XXX', force=True)
relax> residue.name(':2', 'XXX', force=True)
relax> residue.name(':3', 'XXX', force=True)
```

Alternatively:

```
relax> residue.name(':1,2,3', 'XXX', force=
    True)
```

13.2.160 residue.number



Synopsis

Number the residues.

Defaults

```
residue.number(res_id=None, number=None, force=
    False)
```

Keyword arguments

res_id: The residue ID string corresponding to a single residue.

number: The new residue number.

force: A flag which if True will cause the residue to be renumbered.

Description

This simply allows residues to be numbered. The new number cannot correspond to an existing residue.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>, <res_id>, ...] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

Prompt examples

The following sequence of commands will renumber the sequence {1 ALA, 2 GLY, 3 LYS} to {101 ALA, 102 GLY, 103 LYS}:

```
relax> residue.number(':1', 101, force=True)  
relax> residue.number(':2', 102, force=True)  
relax> residue.number(':3', 103, force=True)
```

13.2.161 results.display



Synopsis

Display the results.

Defaults

```
results.display()
```

Description

This will print to screen (STDOUT) the results contained within the current data pipe.

13.2.162 results.read



Synopsis

Read the contents of a relax results file into the relax data store.

Defaults

```
results.read(file='results', dir=None)
```

Keyword arguments

file: The name of the file to read results from.

dir: The directory where the file is located.

Description

This is able to handle uncompressed, bzip2 compressed files, or gzip compressed files automatically. The full file name including extension can be supplied, however, if the file cannot be found the file with ‘.bz2’ appended followed by the file name with ‘.gz’ appended will be searched for.

13.2.163 results.write



Synopsis

Write the results to a file.

Defaults

```
results.write(file='results', dir='pipe_name', compress_type=1, force=False)
```

Keyword arguments

file: The name of the file to output results to. The default is ‘results’. Optionally this can be a file object, or any object with a write() method.

dir: The directory name.

compress_type: The type of compression to use when creating the file.

force: A flag which if True will cause the results file to be overwritten.

Description

This will write the entire contents of the current data pipe into an XML formatted file. This results file can then be read back into relax at a later point in time, or transferred to another machine. This is in contrast to the state.save user function whereby the entire data store, including all data pipes, are saved into a similarly XML formatted file.

To place the results file in the current working directory in the prompt and scripting modes, leave the directory unset. If the directory is set to the special name ‘pipe_name’, then the results file will be placed into a directory with the same name as the current data pipe.

The default behaviour of this function is to compress the file using bzip2 compression. If the extension ‘.bz2’ is not included in the file name, it will be added. The compression can, however, be changed to either no compression or gzip compression. This is controlled by the compression type which can be set to

- 0** – No compression (no file extension),
- 1** – bzip2 compression (‘.bz2’ file extension),
- 2** – gzip compression (‘.gz’ file extension).

The complementary read function will automatically handle the compressed files.

13.2.164 script**Synopsis**

Execute a relax script.

Defaults

`script(file=None, dir=None)`

Keyword arguments

`file`: The name of the file containing the relaxation data.

`dir`: The directory where the file is located.

Description

This will execute a relax or any ordinary Python script.

13.2.165 select.all**Synopsis**

Select all spins in the current data pipe.

Defaults

`select.all()`

Description

This will select all spins, regardless of their current state.

Prompt examples

To select all spins, simply type:

`relax> select.all()`

13.2.166 select.domain



To select all spins of the domain ‘N-dom’, preserving the current selections, simply type one of:

```
relax> select.domain('N-dom', 'AND', True)
```

```
relax> select.domain(domain_id='N-dom',
                      boolean='AND', change_all=True)
```

Synopsis

Select all spins and interatomic data containers of a domain.

Defaults

```
select.domain(domain_id=None, boolean='AND',
              change_all=True)
```

Keyword arguments

domain_id: The domain ID string of the domain to select.

boolean: The boolean operator specifying how interatomic data containers should be selected.

change_all: A flag specifying if all non-matching spin and interatomic data containers should be deselected.

Description

This will select all spins and interatomic data containers of a given domain. This is defined by the domain ID string as specified by the previously executed domain-related user functions.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

Prompt examples

To select all spins of the domain ‘N-dom’, simply type one of:

```
relax> select.domain('N-dom', change_all=
                      True)
```

```
relax> select.domain(domain_id='N-dom',
                      change_all=True)
```

Prompt examples

13.2.167 select.interatom



Synopsis

Select specific interatomic data containers.

To select all N-H backbone bond vectors of a protein, assuming these interatomic data containers have been already set up, type one of:

```
relax> select.interatom('ON', 'OH')
```

```
relax> select.interatom(spin_id1='ON',
                           spin_id2='OH')
```

Defaults

```
select.interatom(spin_id1=None, spin_id2=None,
                 boolean='OR', change_all=False)
```

To select all H-H interatomic vectors of a small organic molecule, type one of:

```
relax> select.interatom('OH*', 'OH*')
```

```
relax> select.interatom(spin_id1='OH*',
                           spin_id2='OH*')
```

Keyword arguments

spin_id1: The spin ID string of the first spin of the interatomic data container.

spin_id2: The spin ID string of the second spin of the interatomic data container.

boolean: The boolean operator specifying how interatomic data containers should be selected.

change_all: A flag specifying if all other interatomic data containers should be changed.

Description

This is used to select specific interatomic data containers which store information about spin pairs such as RDCs, NOEs, dipole-dipole pairs involved in relaxation, etc. The ‘`change_all`’ flag default is `False` meaning that all interatomic data containers currently either selected or deselected will remain that way. Setting this to `True` will cause all interatomic data containers not specified by the spin ID strings to be selected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘`OR`’, ‘`NOR`’, ‘`AND`’, ‘`NAND`’, ‘`XOR`’, ‘`XNOR`’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

13.2.168 select.read



Synopsis

Select the spins contained in a file.

Defaults

```
select.read(file=None, dir=None, spin_id_col=None,
mol_name_col=None, res_num_col=None, res_name_col=
None, spin_num_col=None, spin_name_col=None, sep=
None, spin_id=None, boolean='OR', change_all=False)
```

Keyword arguments

file: The name of the file containing the list of spins to select.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

sep: The column separator (the default is white space).

spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

boolean: The boolean operator specifying how spins should be selected.

change_all: A flag specifying if all other spins should be changed.

Description

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number, residue name,

spin number and/or spin name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID string can be used to restrict the reading to certain spin types, for example only 15N spins when only residue information is in the file.

Empty lines and lines beginning with a hash are ignored.

The ‘`change_all`’ flag default is False meaning that all spins currently either selected or deselected will remain that way. Setting this to True will cause all spins not specified in the file to be deselected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

Prompt examples

To select all residues listed with residue numbers in the first column of the file ‘isolated_peaks’, type one of:

```
relax> select.read('isolated_peaks',
res_num_col=1)
```

```
relax> select.read(file='isolated_peaks',
res_num_col=1)
```

To select the spins in the second column of the relaxation data file ‘r1.600’ while deselecting all other spins, for example type:

```
relax> select.read('r1.600', spin_num_col=2,
change_all=True)
```

```
relax> select.read(file='r1.600',
spin_num_col=2, change_all=True)
```

13.2.169 select.reverse**Synopsis**

Reversal of the spin selection for the given spins.

Defaults

```
select.reverse(spin_id=None)
```

Keyword arguments

spin_id: The spin ID string.

Description

By supplying the spin ID string, a subset of spins can have their selection status reversed.

Prompt examples

To select all currently deselected spins and deselect those which are selected type:

```
relax> select.reverse()
```

**13.2.170 select.spin****Synopsis**

Select specific spins.

Defaults

```
select.spin(spin_id=None, boolean='OR', change_all=False)
```

Keyword arguments

spin_id: The spin ID string.

boolean: The boolean operator specifying how spins should be selected.

change_all: A flag specifying if all other spins should be changed.

Description

The ‘change all’ flag default is False meaning that all spins currently either selected or deselected will remain that way. Setting this to True will cause all spins not specified by the spin ID string to be selected.

Boolean operators

The boolean operator can be used to change how spin systems or interatomic data containers are selected. The allowed values are: ‘OR’, ‘NOR’, ‘AND’, ‘NAND’, ‘XOR’, ‘XNOR’. The following table details how the selections will occur for the different boolean operators.

Please see Table 13.1 on page 253.

Prompt examples

To select only glycines and alanines, assuming they have been loaded with the names GLY and ALA, type one of:

```
relax> select.spin(spin_id=':GLY|:ALA')
```

To select residue 5 CYS in addition to the currently selected residues, type one of:

```
relax> select.spin(':5')
```

```
relax> select.spin(':5&:CYS')
```

```
relax> select.spin(spin_id=':5&:CYS')
```

13.2.171 sequence.attach_protons**Synopsis**

Attach protons to all heteronuclei.

Defaults

`sequence.attach_protons()`

Description

This can be used to attach protons to all the heteronuclei in the current data pipe. For each proton, a spin container will be created.

Prompt examples

To attach protons, simply type:

```
relax> sequence.attach_protons()
```

13.2.172 sequence.copy**Synopsis**

Copy the molecule, residue, and spin sequence data from one data pipe to another.

Defaults

`sequence.copy(pipe_from=None, pipe_to=None, empty=True)`

Keyword arguments

`pipe_from`: The name of the data pipe to copy the sequence data from.

`pipe_to`: The name of the data pipe to copy the sequence data to.

`empty`: A flag which if True will create a molecule, residue, and spin sequence in the target pipe lacking all of the spin data of the source pipe. If False, then the spin data will also be copied.

Description

This will copy the sequence data between data pipes. The destination data pipe must not contain any sequence data. If the source and destination pipes are not specified, then both will default to the current data pipe (hence providing one is essential).

Prompt examples

To copy the sequence from the data pipe ‘m1’ to the current data pipe, type:

```
relax> sequence.copy('m1')
```

```
relax> sequence.copy(pipe_from='m1')
```

To copy the sequence from the current data pipe to the data pipe ‘m9’, type:

```
relax> sequence.copy(pipe_to='m9')
```

To copy the sequence from the data pipe ‘m1’ to ‘m2’, type:

```
relax> sequence.copy('m1', 'm2')
```

```
relax> sequence.copy(pipe_from='m1', pipe_to='m2')
```



13.2.173 sequence.display**Synopsis**

Display sequences of molecules, residues, and/or spins.

Defaults

```
sequence.display(sep=None, mol_name_flag=True,
res_num_flag=True, res_name_flag=True, spin_num_flag=
True, spin_name_flag=True)
```

Keyword arguments

sep: The column separator (the default of None corresponds to white space).

mol_name_flag: A flag which if True will cause the molecule name column to be shown.

res_num_flag: A flag which if True will cause the residue number column to be shown.

res_name_flag: A flag which if True will cause the residue name column to be shown.

spin_num_flag: A flag which if True will cause the spin number column to be shown.

spin_name_flag: A flag which if True will cause the spin name column to be shown.

Description

This will print out the sequence information of all loaded spins in the current data pipe.

13.2.174 sequence.read**Synopsis**

Read the molecule, residue, and spin sequence from a file.

Defaults

```
sequence.read(file=None, dir=None, spin_id_col=None,
mol_name_col=None, res_num_col=None, res_name_col=
None, spin_num_col=None, spin_name_col=None, sep=
None, spin_id=None)
```

Keyword arguments

file: The name of the file containing the sequence data.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

sep: The column separator (the default is white space).

spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

Description

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number, residue name, spin number and/or spin name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID string can be used to restrict the reading to certain spin types, for example only 15N spins when only residue information is in the file.

Prompt examples

The following commands will read protein backbone 15N sequence data out of a file called ‘seq’ where the residue numbers and names are in the first and second columns respectively:

```
relax> sequence.read('seq')

relax> sequence.read('seq', res_num_col=1,
                      res_name_col=2)

relax> sequence.read(file='seq', res_num_col
                      =1, res_name_col=2, sep=None)
```

The following commands will read the residue sequence out of the file ‘noe.out’ which also contains the NOE values:

```
relax> sequence.read('noe.out')

relax> sequence.read('noe.out', res_num_col
                      =1, res_name_col=2)

relax> sequence.read(file='noe.out',
                      res_num_col=1, res_name_col=2)
```

The following commands will read the sequence out of the file ‘noe.600.out’ where the residue numbers are in the second column, the names are in the sixth column and the columns are separated by commas:

```
relax> sequence.read('noe.600.out',
                      res_num_col=2, res_name_col=6, sep=',,')

relax> sequence.read(file='noe.600.out',
                      res_num_col=2, res_name_col=6, sep=',,')
```

The following commands will read the RNA residues and atoms (including C2, C5, C6, C8, N1, and N3) from the file ‘500.NOE’, where the residue number, residue name, spin number, and spin name are in the first to fourth columns respectively:

```
relax> sequence.read('500.NOE', res_num_col
                      =1, res_name_col=2, spin_num_col=3,
                      spin_name_col=4)

relax> sequence.read(file='500.NOE',
                      res_num_col=1, res_name_col=2,
                      spin_num_col=3, spin_name_col=4)
```

13.2.175 sequence.write



Synopsis

Write the molecule, residue, and spin sequence to a file.

Defaults

```
sequence.write(file=None, dir=None, sep=None,
               mol_name_flag=True, res_num_flag=True, res_name_flag=
               True, spin_num_flag=True, spin_name_flag=True, force=
               False)
```

Keyword arguments

file: The name of the file.

dir: The directory name.

sep: The column separator (the default of None corresponds to white space).

mol_name_flag: A flag which if True will cause the molecule name column to be shown.

res_num_flag: A flag which if True will cause the residue number column to be shown.

res_name_flag: A flag which if True will cause the residue name column to be shown.

spin_num_flag: A flag which if True will cause the spin number column to be shown.

spin_name_flag: A flag which if True will cause the spin name column to be shown.

force: A flag which if True will cause the file to be overwritten.

Description

Write the sequence data to file. If no directory name is given, the file will be placed in the current working directory.

13.2.176 spectrometer.frequency ω **Synopsis**

Set the spectrometer proton frequency of the experiment.

Defaults

```
spectrometer.frequency(id=None, frq=None, units='Hz')
```

Keyword arguments

id: The experiment identification string to set the frequency of.

frq: The spectrometer frequency. See the ‘**sfrq**’ parameter in the Varian procpar file or the ‘**SF01**’ parameter in the Bruker acqus file.

units: The units of frequency.

Description

This allows the spectrometer frequency of a given experiment to be set. The expected units are that of the proton resonance frequency in Hertz. See the ‘**sfrq**’ parameter in the Varian procpar file or the ‘**SF01**’ parameter in the Bruker acqus file for the exact value.

13.2.177 spectrometer-temperature**Synopsis**

Specify the temperature of an experiment.

Defaults

```
spectrometer.temperature(id=None, temp=None)
```

Keyword arguments

id: The experiment identification string.

temp: The temperature of the experiment in Kelvin.

Description

This allows the temperature of an experiment to be set. This value should be in Kelvin. In certain analyses, for example those which use pseudocontact shift data, knowledge of the temperature is essential. For the pseudocontact shift, the experiment ID string should match one of the alignment IDs.

13.2.178 spectrum.baseplane_rmsd
**Synopsis**

Set the baseplane RMSD of a given spin in a spectrum for error analysis.

Defaults

```
spectrum.baseplane_rmsd(error=0.0, spectrum_id=None,
                           spin_id=None)
```

Keyword arguments

error: The baseplane RMSD error value.

spectrum_id: The spectrum ID string.

spin_id: The spin ID string.

Description

The spectrum ID identifies the spectrum associated with the error and must correspond to a previously loaded set of intensities. If the spin ID is unset, then the error value for all spins will be set to the supplied value.

13.2.179 spectrum.delete
**Synopsis**

Delete the spectral data corresponding to the spectrum ID string.

Defaults

```
spectrum.delete(spectrum_id=None)
```

Keyword arguments

spectrum_id: The unique spectrum ID string.

Description

The spectral data corresponding to the given spectrum ID string will be removed from the current data pipe.

Prompt examples

To delete the peak height data corresponding to the ID 'R1 ncyc5', type:

```
relax> spectrum.delete('R1 ncyc5')
```

13.2.180 spectrum.error_analysis



Synopsis

Perform an error analysis for peak intensities.

Defaults

`spectrum.error_analysis(subset=None)`

Keyword arguments

`subset`: The list of spectrum ID strings to restrict the error analysis to.

Description

This user function must only be called after all peak intensities have been loaded and all other necessary spectral information set. This includes the baseplane RMSD and the number of points used in volume integration, both of which are only used if spectra have not been replicated.

The error analysis can be restricted to a subset of the loaded spectral data. This is useful, for example, if half the spectra have been collected on one spectrometer and the other half on a different spectrometer.

Six different types of error analysis are supported depending on whether peak heights or volumes are supplied, whether noise is determined from replicated spectra or the RMSD of the baseplane noise, and whether all spectra or only a subset have been duplicated. These are:

Please see Table 13.21 on page 377.

Peak heights with baseplane noise RMSD

When none of the spectra have been replicated, then the peak height errors are calculated using the RMSD of the baseplane noise, the value of which is set by the `spectrum.baseplane_rmsd` user function. This results in a different error per peak per spectrum. The standard deviation error measure for the peak height, `sigma_I`, is set to the RMSD value.

Peak heights with partially replicated spectra

When spectra are replicated, the variance for a single spin at a single replicated spectra set is calculated by the formula

$$\text{sigma}^2 = \text{sum}(\{\text{I}_i - \text{I}_{\text{av}}\}^2) / (n - 1),$$

where sigma^2 is the variance, sigma is the standard deviation, n is the size of the replicated spectra set with i being the corresponding index, I_i is the peak intensity for spectrum i , and I_{av} is the mean over all spectra i.e. the sum of all peak intensities divided by n .

As the value of n in the above equation is always very low since normally only a couple of spectra are collected per replicated spectra set, the variance of all spins is averaged for a single replicated spectra set. Although this results in all spins having the same error, the accuracy of the error estimate is significantly improved.

If there are in addition to the replicated spectra loaded peak intensities which only consist of a single spectrum, i.e. not all spectra are replicated, then the variances of replicated spectra sets will be averaged. This will be used for the entire experiment so that there will be only a single error value for all spins and for all spectra.

Peak heights with all spectra replicated

If all spectra are collected in duplicate (triplicate or higher number of spectra are supported), the each replicated spectra set will have its own error estimate. The error for a single peak is calculated as when partially replicated spectra are collected, and these are again averaged to give a single error per replicated spectra set. However as all replicated spectra sets will have their own error estimate, variance averaging across all spectra sets will not be performed.

Peak volumes with baseplane noise RMSD

The method of error analysis when no spectra have been replicated and peak volumes are used is highly dependent on the integration method. Many methods simply sum the number of points within a fixed region, either a box or oval object. The number of points used, N , must be specified by another user function in this class. Then the error is simply given by the sum of variances:

$$\text{sigma_vol}^2 = \text{sigma_i}^2 * N,$$

where sigma_vol is the standard deviation of the volume, sigma_i is the standard deviation of a single point assumed to be equal to the RMSD of the baseplane noise, and N is the total number of points used in the summation integration method. For a box integration method,

Table 13.21: The six peak intensity error analysis types.

Int type	Noise source	Error scope
Heights	RMSD baseplane	One sigma per peak per spectrum
Heights	Partial duplicate + variance averaging	One sigma for all peaks, all spectra
Heights	All replicated + variance averaging	One sigma per replicated spectra set
Volumes	RMSD baseplane	One sigma per peak per spectrum
Volumes	Partial duplicate + variance averaging	One sigma for all peaks, all spectra
Volumes	All replicated + variance averaging	One sigma per replicated spectra set

this converts to the Nicholson, Kay, Baldissari, Arango, Young, Bax, and Torchia (1992) Biochemistry, 31: 5253-5263 equation:

$$\text{sigma_vol} = \text{sigma_i} * \sqrt{n*m},$$



I

where n and m are the dimensions of the box. Note that a number of programs, for example peakint (http://hugin.ethz.ch/wuthrich/software/xeasy/xeasy_m15.html) does not use all points within the box. And if the number N can not be determined, this category of error analysis is not possible.

Also note that non-point summation methods, for example when line shape fitting is used to determine peak volumes, the equations above cannot be used. Hence again this category of error analysis cannot be used. This is the case for one of the three integration methods used by Sparky (<http://www.cgl.ucsf.edu/home/sparky/manual/peaks.htm#Integration>). And if fancy techniques are used, for example as Cara does to deconvolute overlapping peaks (<http://www.cara.ethz.ch/Wiki/Integration>), this again makes this error analysis impossible.

Peak volumes with partially replicated spectra

When peak volumes are measured by any integration method and a few of the spectra are replicated, then the intensity errors are calculated identically as described in the ‘Peak heights with partially replicated spectra’ section above.

Peak volumes with all spectra replicated

With all spectra replicated and again using any integration methodology, the intensity errors can be calculated as described in the ‘Peak heights with all spectra replicated’ section above.

13.2.181 spectrum.integration-points

Synopsis

Set the number of summed points used in volume integration of a given spin in a spectrum.

Defaults

`spectrum.integration_points(N=None, spectrum_id=None, spin_id=None)`

Keyword arguments

`N`: The number of points used by the summation volume integration method.

`spectrum_id`: The spectrum ID string.

`spin_id`: Restrict setting the number to certain spins.

Description

For a complete description of which integration methods and how many points N are used for different integration techniques, please see the `spectrum.error_analysis` user function documentation.

The spectrum ID identifies the spectrum associated with the value of N and must correspond to a previously loaded set of intensities. If the spin ID is unset, then the number of summed points for all spins will be set to the supplied value.

13.2.182 spectrum.read_intensities



Synopsis

Read peak intensities from a file.

Defaults

```
spectrum.read_intensities(file=None, dir=None,
spectrum_id=None, dim=1, int_method='height', int_col=
None, spin_id_col=None, mol_name_col=None,
res_num_col=None, res_name_col=None, spin_num_col=
None, spin_name_col=None, sep=None, spin_id=None,
ncproc=None)
```

Keyword arguments

file: The name of the file containing the intensity data.

dir: The directory where the file is located.

spectrum_id: The unique spectrum ID string or list of strings to associate with the peak intensity values. If ‘auto’ is provided for a NMRPipe seriesTab formatted file, the IDs are auto generated in form of Z_A{i}.

dim: Associate the data with the spins of any dimension in the peak list. This defaults to w1, the heteronucleus in HSQC type experiments.

int_method: The method by which peaks were integrated.

int_col: The optional column containing the peak intensity data (used by the generic intensity file format, or if the intensities are in a non-standard column).

spin_id_col: The spin ID string column used by the generic intensity file format (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column used by the generic intensity file format (alternative to the spin ID column).

res_num_col: The residue number column used by the generic intensity file format (alternative to the spin ID column).

res_name_col: The residue name column used by the generic intensity file format (alternative to the spin ID column).

spin_num_col: The spin number column used by the generic intensity file format (alternative to the spin ID column).

spin_name_col: The spin name column used by the generic intensity file format (alternative to the spin ID column).

sep: The column separator used by the generic intensity format (the default is white space).

spin_id: The spin ID string used to restrict the loading of data to certain spin subsets.

ncproc: The Bruker specific FID intensity scaling factor.

Description

The peak intensity can either be from peak heights or peak volumes.

The spectrum ID is a label which is subsequently utilised by other user functions. If this identifier matches that of a previously loaded set of intensities, then this indicates a replicated spectrum.

The spectral dimension is used to specify if the intensity data should be loaded into the spins identified by the first dimension w1, second dimension w2, etc.

The integration method is required for the subsequent error analysis. When peak heights are measured, this should be set to ‘height’. Volume integration methods are a bit varied and hence two values are accepted. If the volume integration involves pure point summation, with no deconvolution algorithms or other methods affecting peak heights, then the value should be set to ‘point sum’. All other volume integration methods, e.g. line shape fitting, the value should be set to ‘other’.

If a series of intensities extracted from Bruker FID files processed in Topspin or XWinNMR are to be compared, the ncproc parameter may need to be supplied. This is because this FID is stored using integer representation and is scaled using ncproc to avoid numerical truncation artifacts. If two spectra have significantly different maximal intensities, then ncproc will be different for both. The intensity scaling is binary, i.e. $2^{**\text{ncproc}}$. Therefore if spectrum A has an ncproc of 6 and spectrum B a value of 7, then a reference intensity in B will be double that of A. Internally, relax stores the intensities scaled by $2^{**\text{ncproc}}$.

File formats

The peak list or intensity file will be automatically determined.

Sparky peak list: The file should be a Sparky peak list saved after typing the command ‘lt’. The default is to assume that columns 0, 1, 2, and 3 (1st, 2nd, 3rd, and 4th) contain the Sparky assignment, w1, w2, and peak intensity data respectively. The frequency data w1 and w2 are ignored while the peak intensity data can either be the peak height or volume displayed by changing the window options. If the peak intensity data is not within column 3, set the integration column to the appropriate number (column numbering starts from 0 rather than 1).

XEasy peak list: The file should be the saved XEasy text window output of the list peak entries command, ‘tw’ followed by ‘1e’. As the columns are fixed, the peak intensity column is hardwired to number 10 (the 11th column) which contains either the peak height or peak volume data. Because the columns are fixed, the integration column number will be ignored.

NMRView: The file should be a NMRView peak list. The default is to use column 16 (which contains peak heights) for peak intensities. To use peak volumes (or evolumes), int_col must be set to 15.

NMRPipe seriesTab: The file should be a NMRPipe-format Spectral Series list. If the spectrum_id=‘auto’, the IDs are auto generated in form of Z-A{i}.

Generic intensity file: This is a generic format which can be created by scripting to support non-supported peak lists. It should contain in the first few columns enough information to identify the spin. This can include columns for the molecule name, residue number, residue name, spin number, and spin name. Alternatively a spin ID string column can be used. The peak intensities can be placed in another column specified by the integration column number. Intensities from multiple spectra can be placed into different columns, and these can then be specified simultaneously by setting the integration column value to a list of columns. This list must be matched by setting the spectrum ID to a list of the same length. If columns are delimited by a character other than whitespace, this can be specified with the column separator. The spin ID can be used to restrict the loading to specific spin subsets.

Prompt examples

To read the reference and saturated spectra peak heights from the Sparky formatted files ‘ref.list’ and ‘sat.list’, type:

```
relax> spectrum.read_intensities(file='ref.list', spectrum_id='ref')

relax> spectrum.read_intensities(file='sat.list', spectrum_id='sat')
```

To read the reference and saturated spectra peak heights from the XEasy formatted files ‘ref.text’ and ‘sat.text’, type:

```
relax> spectrum.read_intensities(file='ref.text', spectrum_id='ref')

relax> spectrum.read_intensities(file='sat.text', spectrum_id='sat')
```

13.2.183 spectrum.replicated



Synopsis

Specify which spectra are replicates of each other.

Defaults

spectrum.replicated(spectrum_ids=None)

Keyword arguments

spectrum_ids: The list of replicated spectra ID strings.

Description

This is used to identify which of the loaded spectra are replicates of each other. Specifying the replicates is essential for error analysis if the baseplane RMSD has not been supplied.

Prompt examples

To specify that the NOE spectra labelled ‘ref1’, ‘ref2’, and ‘ref3’ are the same spectrum replicated, type one of:

```
relax> spectrum.replicated(['ref1', 'ref2', 'ref3'])

relax> spectrum.replicated(spectrum_ids=['ref1', 'ref2', 'ref3'])
```

To specify that the two R₂ spectra ‘ncyc2’ and ‘ncyc2b’ are the same time point, type:

```
relax> spectrum.replicated(['ncyc2', 'ncyc2b'])
```

13.2.184 spin.copy**Synopsis**

Copy all data associated with a spin.

Defaults

```
spin.copy(pipe_from=None, spin_from=None, pipe_to=None, spin_to=None)
```

Keyword arguments

pipe_from: The data pipe containing the spin from which the data will be copied. This defaults to the current data pipe.

spin_from: The spin identifier string of the spin to copy the data from.

pipe_to: The data pipe to copy the data to. This defaults to the current data pipe.

spin_to: The spin identifier string of the spin to copy the data to. If left blank, the new spin will have the same name as the old.

Description

This will copy all the data associated with the identified spin to the new, non-existent spin. The new spin must not already exist.

Prompt examples

To copy the spin data from spin 1 to the new spin 2, type:

```
relax> spin.copy(spin_from='@1', spin_to='@2')
```

To copy spin 1 of the molecule ‘Old mol’ to spin 5 of the molecule ‘New mol’, type:

```
relax> spin.copy(spin_from='#Old mol@1', spin_to='#New mol@5')
```

To copy the spin data of spin 1 from the data pipe ‘m1’ to ‘m2’, assuming the current data pipe is ‘m1’, type:

```
relax> spin.copy(spin_from='@1', pipe_to='m2')
```

```
relax> spin.copy(pipe_from='m1', spin_from='@1', pipe_to='m2', spin_to='@1')
```

13.2.185 spin.create**Synopsis**

Create a new spin.

Defaults

```
spin.create(spin_name=None, spin_num=None, res_name=None, res_num=None, mol_name=None)
```

Keyword arguments

spin_name: The name of the spin.

spin_num: The spin number.

res_name: The name of the residue to add the spin to.

res_num: The number of the residue to add the spin to.

mol_name: The name of the molecule to add the spin to.

Description

This will add a new spin data container to the relax data storage object. The same spin number cannot be used more than once.

Prompt examples

The following sequence of commands will add the spins 1 C4, 2 C9, 3 C15 to residue number 10:

```
relax> spin.create('C4', 1, res_num=10)
```

```
relax> spin.create('C9', 2, res_num=10)
```

```
relax> spin.create('C15', 3, res_num=10)
```

13.2.186 spin.create_pseudo



Synopsis

Create a spin system representing a pseudo-atom.

Defaults

```
spin.create_pseudo(spin_name=None, spin_num=None,
res_id=None, members=None, averaging='linear')
```

Keyword arguments

spin_name: The name of the pseudo-atom spin.

spin_num: The spin number.

res_id: The molecule and residue ID string identifying the position to add the pseudo-spin to.

members: A list of the atoms (as spin ID strings) that the pseudo-atom is composed of.

averaging: The positional averaging technique.

Description

This will create a spin data container representing a number of pre-existing spin containers as a pseudo-atom. The optional spin number must not already exist.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the 'Q' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not

contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

Prompt examples

The following will create the pseudo-atom named 'Q9' consisting of the protons '@H16', '@H17', '@H18':

```
relax> spin.create_pseudo('Q9', members=['@H16', '@H17', '@H18'])
```

13.2.187 spin.delete**Synopsis**

Delete spins.

Defaults

spin.delete(spin_id=None)

Keyword arguments

spin_id: The spin identifier string.

Description

This can be used to delete a single or sets of spins. See the identification string documentation below for more information.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.188 spin.display**Synopsis**

Display information about the spin(s).

Defaults

spin.display(spin_id=None)

Keyword arguments

spin_id: The spin identification string.

Description

This will display the spin data loaded into the current data pipe.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.



Prompt examples

13.2.189 spin.element



The set all spins of residue 1 to be carbons, type one of:

```
relax> spin.element('@1', 'C', force=True)

relax> spin.element(spin_id='@1', element='C
', force=True)
```

Synopsis

Set the element type of the spin.

Defaults

```
spin.element(element=None, spin_id=None, force=False)
```

Keyword arguments

element: The IUPAC element name.

spin_id: The spin identification string corresponding to one or more spins.

force: A flag which if True will cause the element to be changed.

Description

This allows the element type of the spins to be set.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the '.' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>, <res_id>, ...] @<atom_id>[, <atom_id>, <atom_id>, ...]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

Prompt examples

13.2.190 spin.isotope



The set all spins of residue 1 to the ‘`13C`’ nuclear isotope, type one of:

```
relax> spin.isotope('@1', '13C', force=True)

relax> spin.isotope(spin_id='@1', isotope='
13C', force=True)
```

Synopsis

Set the spins’ nuclear isotope type.

Defaults

```
spin.isotope(isotope=None, spin_id=None, force=False)
```

Keyword arguments

`isotope`: The nuclear isotope name in the AE notation - the atomic mass number followed by the element symbol.

`spin_id`: The spin identification string corresponding to one or more spins.

`force`: A flag which if True will cause the nuclear isotope to be changed.

Description

This allows the nuclear isotope type of the spins to be set.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the ‘#’ character, the residue ID token beginning with the ‘:’ character, and the atom or spin system ID token beginning with the ‘@’ character. Each token can be composed of multiple elements - one per spin - separated by the ‘,’ character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the ‘-’ character. Negative numbers are supported. The full ID string specification is ‘`#<mol_name> :<res_id>[, <res_id>[, <res_id>, ...]] @<atom_id>[, <atom_id>[, <atom_id>, ...]]`’, where the token elements are ‘`<mol_name>`’, the name of the molecule, ‘`<res_id>`’, the residue identifier which can be a number, name, or range of numbers, ‘`<atom_id>`’, the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the ‘#’ character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string ‘`@H*`’ will select the protons ‘`H`’, ‘`H2`’, ‘`H98`’.

13.2.191 spin.name



Regular expression can be used to select spins. For example the string ‘@H*’ will select the protons ‘H’, ‘H2’, ‘H98’.

Synopsis

Name the spins.

Defaults

```
spin.name(name=None, spin_id=None, force=False)
```

Keyword arguments

name: The new name.

spin_id: The spin identification string corresponding to one or more spins.

force: A flag which if True will cause the spin to be renamed.

Description

This simply allows spins to be named (or renamed). Spin naming often essential. For example when reading Sparky peak list files, then the spin name must match that in the file.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the ‘#’ character, the residue ID token beginning with the ‘:’ character, and the atom or spin system ID token beginning with the ‘@’ character. Each token can be composed of multiple elements - one per spin - separated by the ‘,’ character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the ‘-’ character. Negative numbers are supported. The full ID string specification is ‘#@<mol_name> :<res_id>[, <res_id>, <res_id>, ...]’ ‘@<atom_id>[, <atom_id>, <atom_id>, ...]’, where the token elements are ‘<mol_name>’, the name of the molecule, ‘<res_id>’, the residue identifier which can be a number, name, or range of numbers, ‘<atom_id>’, the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the ‘#’ character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Prompt examples

The following sequence of commands will rename the sequence {1 C1, 2 C2, 3 C3} to {1 C11, 2 C12, 3 C13}:

```
relax> spin.name('@1', 'C11', force=True)
```

```
relax> spin.name('@2', 'C12', force=True)
```

```
relax> spin.name('@3', 'C13', force=True)
```

Prompt examples

13.2.192 spin.number



The following sequence of commands will renumber the sequence {1 C1, 2 C2, 3 C3} to {-1 C1, -2 C2, -3 C3}:

```
relax> spin.number('@1', -1, force=True)
relax> spin.number('@2', -2, force=True)
relax> spin.number('@3', -3, force=True)
```

Synopsis

Number the spins.

Defaults

```
spin.number(spin_id=None, number=None, force=False)
```

Keyword arguments

spin_id: The spin identification string corresponding to a single spin.

number: The new spin number.

force: A flag which if True will cause the spin to be renumbered.

Description

This simply allows spins to be numbered. The new number cannot correspond to an existing spin number.

Spin ID string documentation

The identification string is composed of three components: the molecule ID token beginning with the '#' character, the residue ID token beginning with the ':' character, and the atom or spin system ID token beginning with the '@' character. Each token can be composed of multiple elements - one per spin - separated by the ',' character and each individual element can either be a number (which must be an integer, in string format), a name, or a range of numbers separated by the '-' character. Negative numbers are supported. The full ID string specification is '#<mol_name> :<res_id>[, <res_id>, <res_id>, ...] @<atom_id>[, <atom_id>[, <atom_id>, ...]]', where the token elements are '<mol_name>', the name of the molecule, '<res_id>', the residue identifier which can be a number, name, or range of numbers, '<atom_id>', the atom or spin system identifier which can be a number, name, or range of numbers.

If one of the tokens is left out then all elements will be assumed to match. For example if the string does not contain the '#' character then all molecules will match the string. If only the molecule ID component is specified, then all spins of the molecule will match.

Regular expression can be used to select spins. For example the string '@H*' will select the protons 'H', 'H2', 'H98'.

13.2.193 state.load**Synopsis**

```
Load a saved program state.
```

Defaults

```
state.load(state='state.bz2', dir=None, force=False)
```

Keyword arguments

state: The file name, which can be a string or a file descriptor object, of a saved program state.

dir: The name of the directory in which the file is found.

force: A boolean flag which if True will cause the current program state to be overwritten.

Description

This is able to handle uncompressed, bzip2 compressed files, or gzip compressed files automatically. The full file name including extension can be supplied, however, if the file cannot be found, this function will search for the file name with ‘.bz2’ appended followed by the file name with ‘.gz’ appended.

For more advanced users, file descriptor objects are supported. If the force flag is set to True, then the relax data store will be reset prior to the loading of the saved state.

Prompt examples

The following commands will load the state saved in the file ‘save’.

```
relax> state.load('save')
relax> state.load(state='save')
```

Use one of the following commands to load the state saved in the bzip2 compressed file ‘save.bz2’:

```
relax> state.load('save')
relax> state.load(state='save')
relax> state.load('save.bz2')
relax> state.load(state='save.bz2', force=
    True)
```

13.2.194 state.save**Synopsis**

```
Save the program state.
```

Defaults

```
state.save(state='state.bz2', dir=None, compress_type=1,
force=False)
```

Keyword arguments

state: The file name, which can be a string or a file descriptor object, to save the current program state in.

dir: The name of the directory in which to place the file.

compress_type: The type of compression to use when creating the file.

force: A boolean flag which if set to True will cause the file to be overwritten.

Description

This will place the program state - the relax data store - into a file for later reloading or reference. The default format is an XML formatted file.

The default behaviour of this function is to compress the file using bzip2 compression. If the extension ‘.bz2’ is not included in the file name, it will be added. The compression can, however, be changed to either no compression or gzip compression. This is controlled by the compression type which can be set to

- 0 – No compression (no file extension).
- 1 – bzip2 compression (‘.bz2’ file extension).
- 2 – gzip compression (‘.gz’ file extension).

Prompt examples

The following commands will save the current program state, uncompressed, into the file ‘save’:

```
relax> state.save('save', compress_type=0)
relax> state.save(state='save',
    compress_type=0)
```

The following commands will save the current program state into the bzip2 compressed file ‘`save.bz2`’:

```
relax> state.save('save')

relax> state.save(state='save')

relax> state.save('save.bz2')

relax> state.save(state='save.bz2')
```

If the file ‘`save`’ already exists, the following commands will save the current program state by overwriting the file.

```
relax> state.save('save', force=True)

relax> state.save(state='save', force=True)
```

13.2.195 structure.add_atom



Synopsis

Add an atom.

Defaults

```
structure.add_atom(atom_name=None, res_name=None,
res_num=None, pos=None, element=None, atom_num=
None, chain_id=None, segment_id=None, pdb_record=
None)
```

Keyword arguments

`atom_name`: The atom name.

`res_name`: The residue name.

`res_num`: The residue number.

`pos`: The atomic coordinates.

`element`: The element name.

`atom_num`: The optional atom number.

`chain_id`: The optional chain ID string.

`segment_id`: The optional segment ID string.

`pdb_record`: The optional PDB record name, e.g. ‘`ATOM`’ or ‘`HETATM`’.

Description

This allows atoms to be added to the internal structural object. To use the same atomic coordinates for all models, the atomic position can be an array of 3 values. Alternatively different coordinates can be used for each model if the atomic position is a rank-2 array where the first dimension matches the number of models currently present.

13.2.196 structure.add_model**Synopsis**

Add a new model.

Defaults

`structure.add_model(model_num=None)`

Keyword arguments

`model_num`: The number of the new model.

Description

This allows new models to be added to the internal structural object. Note that no structural information is allowed to be present

13.2.197 structure.connect_atom**Synopsis**

Connect two atoms.

Defaults

`structure.connect_atom(index1=None, index2=None)`

Keyword arguments

`index1`: The global index of the first atom.

`index2`: The global index of the second atom.

Description

This allows atoms to be connected in the internal structural object. The global index is normally equal to the PDB atom number minus 1.

13.2.198 `structure.create_diff_tensor_pdb`



Synopsis

Create a PDB file to represent the diffusion tensor.

Defaults

```
structure.create_diff_tensor_pdb(scale=1.8e-06, file='tensor.pdb', dir=None, force=False)
```

Keyword arguments

scale: Value for scaling the diffusion rates.

file: The name of the PDB file.

dir: The directory to place the file into.

force: A flag which, if set to True, will overwrite the any pre-existing file.

Description

This creates a PDB file containing an artificial geometric structure to represent the diffusion tensor. A structure must have previously been read into relax. The diffusion tensor is represented by an ellipsoidal, spheroidal, or spherical geometric object with its origin located at the centre of mass (of the selected residues). This diffusion tensor PDB file can subsequently read into any molecular viewer.

There are four different types of residue within the PDB. The centre of mass of the selected residues is represented as a single carbon atom of the residue ‘COM’. The ellipsoidal geometric shape consists of numerous H atoms of the residue ‘TNS’. The axes of the tensor, when defined, are presented as the residue ‘AXS’ and consist of carbon atoms: one at the centre of mass and one at the end of each eigenvector. Finally, if Monte Carlo simulations were run and the diffusion tensor parameters were allowed to vary then there will be multiple ‘SIM’ residues, one for each simulation. These are essentially the same as the ‘AXS’ residue, representing the axes of the simulated tensors, and they will appear as a distribution.

As the Brownian rotational diffusion tensor is a measure of the rate of rotation about different axes - the larger the geometric object, the faster the diffusion of a molecule. For example the diffusion tensor of a water molecule is much larger than that of a macromolecule.

The effective global correlation time experienced by an XH bond vector, not to be confused with the Lipari and

Szabo parameter $\tau_{\perp e}$, will be approximately proportional to the component of the diffusion tensor parallel to it. The approximation is not exact due to the multiexponential form of the correlation function of Brownian rotational diffusion. If an XH bond vector is parallel to the longest axis of the tensor, it will be unaffected by rotations about that axis, which are the fastest rotations of the molecule, and therefore its effective global correlation time will be maximal.

To set the size of the diffusion tensor within the PDB frame the unit vectors used to generate the geometric object are first multiplied by the diffusion tensor (which has the units of inverse seconds) then by the scaling factor (which has the units of second Å² and has the default value of 1.8e-6 s·Ångstrom). Therefore the rotational diffusion rate per Å² is equal the inverse of the scale value (which defaults to 5.56e5 s⁻¹·Ångstrom⁻¹). Using the default scaling value for spherical diffusion, the correspondence between global correlation time, \mathfrak{D}_{iso} diffusion rate, and the radius of the sphere for a number of discrete cases will be:

Please see Table 13.22 on page 391.

The scaling value has been fixed to facilitate comparisons within or between publications, but can be changed to vary the size of the tensor geometric object if necessary. Reporting the rotational diffusion rate per Å² within figure legends would be useful.

To create the tensor PDB representation, a number of algorithms are utilised. Firstly the centre of mass is calculated for the selected residues and is represented in the PDB by a C atom. Then the axes of the diffusion are calculated, as unit vectors scaled to the appropriate length (multiplied by the eigenvalue \mathfrak{D}_x , \mathfrak{D}_y , \mathfrak{D}_z , $\mathfrak{D}_{||}$, \mathfrak{D}_{\perp} , or \mathfrak{D}_{iso} as well as the scale value), and a C atom placed at the position of this vector plus the centre of mass. Finally a uniform distribution of vectors on a sphere is generated using spherical coordinates. By incrementing the polar angle using an arccos distribution, a radial array of vectors representing latitude are created while incrementing the azimuthal angle evenly creates the longitudinal vectors. These unit vectors, which are distributed within the PDB frame and are of 1 Å in length, are first rotated into the diffusion frame using a rotation matrix (the spherical diffusion tensor is not rotated). Then they are multiplied by the diffusion tensor matrix to extend the vector out to the correct length, and finally multiplied by the scale value so that the vectors reasonably superimpose onto the macromolecular structure. The last set of algorithms place all this information into a PDB file. The distribution of vectors are represented by H atoms and are all connected using PDB CONECT records. Each H atom is connected to its two neighbours on both the longitude and latitude. This creates a geometric PDB object with longitudinal and latitudinal lines.

Table 13.22: Diffusion tensor PDB representation sizes using the default scaling for different diffusion tensors

τ_m (ns)	\mathfrak{D}_{iso} (s^{-1})	Radius (Å)
1	1.67e8	300
3	5.56e7	100
10	1.67e7	30
30	5.56e6	10

		Description
13.2.199	structure.create_rotor_pdb	This creates a PDB file representation of a rotor motional model. The model axis is defined by a vector and a single point on the axis. The centre of the representation will be taken as the point on the rotor axis closest to the given centre position. The size of the representation is defined by the span, which is the distance from the central point to the rotors, and the length of the blades.
		
Synopsis		
Create a PDB file representation of a rotor.		
Defaults		
structure.create_rotor_pdb (file='rotor.pdb', dir=None, rotor_angle=0.0, axis=None, axis_pt=None, centre=None, span=2e-09, blade_length=5e-10, force=False, staggered=False)		
Keyword arguments		
file: The name of the PDB file.		
dir: The directory to place the file into.		
rotor_angle: The angle of the rotor motion in degrees.		
axis: The vector defining the rotor axis.		
axis_pt: A point lying anywhere on the rotor axis. This is used to define the position of the axis in 3D space.		
centre: The central point of the representation. If this point is not on the rotor axis, then the closest point on the axis will be used for the centre.		
span: The distance from the central point to the rotor blades (meters).		
blade_length: The length of the representative rotor blades.		
force: A flag which if True will overwrite the file if it already exists.		
staggered: A flag which if True will cause the rotor blades to be staggered. This is used to avoid blade overlap.		

13.2.200 structure.create_vector_dist



Synopsis

Create a PDB file representation of the distribution of XH bond vectors.

Defaults

```
structure.create_vector_dist(length=2e-09, file='XH_dist.pdb', dir=None, symmetry=True, force=False)
```

Keyword arguments

length: The length of the vectors in the PDB representation (meters).

file: The name of the PDB file.

dir: The directory to place the file into.

symmetry: A flag which if True will create a second chain with reversed XH bond orientations.

force: A flag which if True will overwrite the file if it already exists.

Description

This creates a PDB file containing an artificial vectors, the length of which default to 20 Å. A structure must have previously been read into relax. The origin of the vector distribution is located at the centre of mass (of the selected residues). This vector distribution PDB file can subsequently be read into any molecular viewer.

Because of the symmetry of the diffusion tensor reversing the orientation of the XH bond vector has no effect. Therefore by setting the symmetry flag two chains ‘A’ and ‘B’ will be added to the PDB file whereby chain ‘B’ is chain ‘A’ with the XH bonds reversed.

13.2.201 structure.delete



Synopsis

Delete structural information.

Defaults

```
structure.delete(atom_id=None)
```

Keyword arguments

atom_id: The atom identification string.

Description

This will delete structural information from the current data pipe. All spin and sequence information loaded from these structures will be preserved - this only affects the structural data. The atom ID argument can be used to restrict deletion to parts of the loaded molecules.

Prompt examples

To delete everything, simply type:

```
relax> structure.delete()
```

To delete residues 50 to 100 of the molecule called ‘Ap4Aase’, type one of:

```
relax> structure.delete(':50-100')
```

```
relax> structure.delete(atom_id=':50-100')
```

Prompt examples

13.2.202 structure.displacement



Synopsis

Determine the rotational and translational displacement between a set of models.

Defaults

```
structure.displacement(model_from=None, model_to=None, atom_id=None, centroid=None)
```

Keyword arguments

model_from: The optional model number for the starting position of the displacement.

model_to: The optional model number for the ending position of the displacement.

atom_id: The atom identification string.

centroid: The alternative position of the centroid.

Description

This user function allows the rotational and translational displacement between two models of the same structure to be calculated. The information will be printed out in various formats and held in the relax data store. This is directional, so there is a starting and ending position for each displacement. If the starting and ending models are not specified, then the displacements in all directions between all models will be calculated.

The atom ID, which uses the same notation as the spin ID strings, can be used to restrict the displacement calculation to certain molecules, residues, or atoms. This is useful if studying domain motions, secondary structure rearrangements, amino acid side chain rotations, etc.

By supplying the position of the centroid, an alternative position than the standard rigid body centre is used as the focal point of the motion. This allows, for example, a pivot of a rotational domain motion to be specified. This is not a formally correct algorithm, all translations will be zero, but does give an indication to the amplitude of the pivoting angle.

To determine the rotational and translational displacements between all sets of models, type:

```
relax> structure.displacement()
```

To determine the displacement from model 5 to all other models, type:

```
relax> structure.displacement(model_from=5)
```

To determine the displacement of all models to model 5, type:

```
relax> structure.displacement(model_to=5)
```

To determine the displacement of model 2 to model 3, type one of:

```
relax> structure.displacement(2, 3)
```

```
relax> structure.displacement(model_from=2, model_to=3)
```

13.2.203 structure.find_pivot**Synopsis**

Find the pivot point of the motion of a set of structures.

Defaults

```
structure.find_pivot(models=None, atom_id=None,
init_pos=None, func_tol=1e-05, box_limit=200)
```

Keyword arguments

models: The list of models to use.

atom_id: The atom identification string.

init_pos: The initial position of the pivot.

func_tol: The function tolerance. This is used to terminate minimisation once the function value between iterations is less than the tolerance. The default value is 1e-5.

box_limit: The pivot point is constrained within a box of +/- x Å using the logarithmic barrier function together with simplex optimisation. This argument is the value of x .

Description

This is used to find pivot point of motion between a set of structural models. If the list of models is not supplied, then all models will be used.

The atom ID, which uses the same notation as the spin ID strings, can be used to restrict the search to certain molecules, residues, or atoms. For example to only use backbone heavy atoms in a protein, use the atom ID of ‘**ON,C,CA,O**’, assuming those are the names of the atoms from the structural file.

By supplying the position of the centroid, an alternative position than the standard rigid body centre is used as the focal point of the superimposition. This allows, for example, the superimposition about a pivot point.

13.2.204 structure.get_pos**Synopsis**

Extract the atomic positions from the loaded structures for the given spins.

Defaults

```
structure.get_pos(spin_id=None, ave_pos=True)
```

Keyword arguments

spin_id: The spin identification string.

ave_pos: A flag specifying if the position of the atom is to be averaged across models.

Description

This allows the atomic positions of the spins to be extracted from the loaded structures. This is automatically performed by the `structure.load_spins` user function, but if the sequence information is generated in other ways, this user function allows the structural information to be obtained.

If averaging the atomic positions, then average position of all models will be loaded into the spin container. Otherwise the positions from all models will be loaded separately.

Prompt examples

For a model-free backbone amide nitrogen analysis whereby the N spins have already been created, to obtain the backbone N positions from the file ‘**1F3Y.pdb**’ (which is a single protein), type the following two user functions:

```
relax> structure.read_pdb('1F3Y.pdb')
```

```
relax> structure.get_pos(spin_id='ON')
```

13.2.205 structure.load_spins



Synopsis

Load spins from the structure into the relax data store.

Defaults

```
structure.load_spins(spin_id=None, mol_name_target=
None, ave_pos=True)
```

Keyword arguments

spin_id: The spin identification string for the selective loading of certain spins into the relax data store.

mol_name_target: The name of target molecule container, overriding the name of the loaded structures.

ave_pos: A flag specifying if the position of the atom is to be averaged across models.

Description

This allows a sequence to be generated within the relax data store using the atomic information from the structure already associated with this data pipe. The spin ID string is used to select which molecules, which residues, and which atoms will be recognised as spin systems within relax. If the spin ID is left unspecified, then all molecules, residues, and atoms will be placed within the data store (and all atoms will be treated as spins).

If averaging the atomic positions, then average position of all models will be loaded into the spin container. Otherwise the positions from all models will be loaded separately.

Prompt examples

For a model-free backbone amide nitrogen analysis, to load just the backbone N sequence from the file ‘1F3Y.pdb’ (which is a single protein), type the following two user functions:

```
relax> structure.read_pdb('1F3Y.pdb')
relax> structure.load_spins(spin_id='@N')
```

For an RNA analysis of adenine C8 and C2, guanine C8 and N1, cytidine C5 and C6, and uracil N3, C5, and C6, type the following series of commands (assuming that the PDB file with this atom naming has already been read):

```
relax> structure.load_spins(spin_id=":@C8")
relax> structure.load_spins(spin_id=":@C2")
relax> structure.load_spins(spin_id=":@C8")
relax> structure.load_spins(spin_id=":@N1")
relax> structure.load_spins(spin_id=":@C5")
relax> structure.load_spins(spin_id=":@C6")
relax> structure.load_spins(spin_id=":@N3")
relax> structure.load_spins(spin_id=":@C5")
relax> structure.load_spins(spin_id=":@C6")
```

Alternatively using some Python programming:

```
relax> for id in [":@C8", ":@C2", ":@C8",
":@N1", ":@C5", ":@C6", ":@N3", ":"@C5", ":@C6"]:
```

```
relax>     structure.load_spins(spin_id=id)
```

13.2.206 structure.read_pdb



Synopsis

Reading structures from PDB files.

Defaults

```
structure.read_pdb(file=None, dir=None, read_mol=
None, set_mol_name=None, read_model=None,
set_model_num=None, alt_loc=None, merge=False)
```

Keyword arguments

file: The name of the PDB file.

dir: The directory where the file is located.

read_mol: If set, only the given molecule(s) will be read. The molecules are numbered consecutively from 1. If unset, then all molecules will be loaded. By providing a list of numbers such as [1, 2], multiple molecules will be read.

set_mol_name: Set the names of the read molecules. If unset, then the molecules will be automatically labelled based on the file name or other information. This can either be a single name or a list of names.

read_model: If set, only the given model number(s) from the PDB file will be read. Otherwise all models will be read. This can be a single number or list of numbers.

set_model_num: Set the model numbers of the loaded molecules. If unset, then the PDB model numbers will be preserved if they exist. This can be a single number or list of numbers.

alt_loc: The PDB ATOM record ‘Alternate location indicator’ field value.

merge: A flag which if set to True will try to merge the PDB structure into the currently loaded structures.

Description

The reading of PDB files into relax is quite a flexible procedure allowing for both models, defined as an ensemble of the same molecule but with different atomic positions, and different molecules within the same model. One of more molecules can exist in one or more models. The flexibility allows PDB models to be converted into different molecules and different PDB files loaded as the same molecule but as different models.

In a PDB file, the models are specified by the MODEL PDB record. All the supported PDB readers in relax recognise this. The internal reader defines molecules using the TER PDB record. In both cases, the molecules will be numbered consecutively from 1.



Setting the molecule name allows the molecule within the PDB (within one model) to have a custom name. If not set, then the molecules will be named after the file name, with the molecule number appended if more than one exists.

Note that relax will complain if it cannot work out what to do.

This is able to handle uncompressed, bzip2 compressed files, or gzip compressed files automatically. The full file name including extension can be supplied, however, if the file cannot be found, this function will search for the file name with ‘.bz2’ appended followed by the file name with ‘.gz’ appended.

If a PDB file contains alternative atomic locations, then the alternate location indicator must be specified to allow one of the multiple coordinate sets to be select.

Prompt examples

To load all structures from the PDB file ‘test.pdb’ in the directory ‘~/pdb’, including all models and all molecules, type one of:

```
relax> structure.read_pdb('test.pdb', '~/pdb')
```

```
relax> structure.read_pdb(file='test.pdb',
    dir='pdb')
```

To load the 10th model from the file ‘test.pdb’ and naming it ‘CaM’, use one of:

```
relax> structure.read_pdb('test.pdb',
    read_model=10, set_mol_name='CaM')
```

```
relax> structure.read_pdb(file='test.pdb',
    read_model=10, set_mol_name='CaM')
```

To load models 1 and 5 from the file ‘test.pdb’ as two different structures of the same model, type one of:

```
relax> structure.read_pdb('test.pdb',
    read_model=[1, 5], set_model_num=[1, 1])
```

```
relax> structure.read_pdb('test.pdb',
    set_mol_name=['CaM_1', 'CaM_2'],
    read_model=[1, 5], set_model_num=[1, 1])
```

To load the files ‘lactose_MCMM4_S1_1.pdb’, ‘lactose_MCMM4_S1_2.pdb’, ‘lactose_MCMM4_S1_3.pdb’ and ‘lactose_MCMM4_S1_4.pdb’ as models, type the following sequence of commands:

```

relax> structure.read_pdb(
    lactose_MCMM4_S1_1.pdb', set_mol_name='
    lactose_MCMM4_S1', set_model_num=1)

relax> structure.read_pdb(
    lactose_MCMM4_S1_2.pdb', set_mol_name='
    lactose_MCMM4_S1', set_model_num=2)

relax> structure.read_pdb(
    lactose_MCMM4_S1_3.pdb', set_mol_name='
    lactose_MCMM4_S1', set_model_num=3)

relax> structure.read_pdb(
    lactose_MCMM4_S1_4.pdb', set_mol_name='
    lactose_MCMM4_S1', set_model_num=4)

```

13.2.207 structure.read_xyz



Synopsis

Reading structures from XYZ files.

Defaults

structure.read_xyz(file=None, dir=None, read_mol=None, set_mol_name=None, read_model=None, set_model_num=None)

Keyword arguments

file: The name of the XYZ file.

dir: The directory where the file is located.

read_mol: If set, only the given molecule(s) will be read. The molecules are numbered consecutively from 1. If unset, then all molecules will be loaded. By providing a list of numbers such as [1, 2], multiple molecules will be read.

set_mol_name: Set the names of the read molecules. If unset, then the molecules will be automatically labelled based on the file name or other information. This can either be a single name or a list of names.

read_model: If set, only the given model number(s) from the PDB file will be read. Otherwise all models will be read. This can be a single number or list of numbers.

set_model_num: Set the model numbers of the loaded molecules. If unset, then the PDB model numbers will be preserved if they exist. This can be a single number or list of numbers.

Description

The XYZ files with different models, which defined as an ensemble of the same molecule but with different atomic positions, can be read into relax. If there are several molecules in one xyz file, please separate them into different files and then load them individually. Loading different models and different molecules is controlled by specifying the molecule number read, setting the molecule names, specifying which model to read, and setting the model numbers.

The setting of molecule names is used to name the molecules within the XYZ (within one model). If not set, then the molecules will be named after the file name, with the molecule number appended if more than one exists.

Note that relax will complain if it cannot work out what to do.

Prompt examples

To load all structures from the XYZ file ‘test.xyz’ in the directory ‘~/xyz’, including all models and all molecules, type one of:

```
relax> structure.read_xyz('test.xyz', '~/xyz
')
```

```
relax> structure.read_xyz(file='test.xyz',
    dir='xyz')
```

To load the 10th model from the file ‘test.xyz’ and naming it ‘CaM’, use one of:

```
relax> structure.read_xyz('test.xyz',
    read_model=10, set_mol_name='CaM')
```

```
relax> structure.read_xyz(file='test.xyz',
    read_model=10, set_mol_name='CaM')
```

To load models 1 and 5 from the file ‘test.xyz’ as two different structures of the same model, type one of:

```
relax> structure.read_xyz('test.xyz',
    read_model=[1, 5], set_model_num=[1,
    1])
```

```
relax> structure.read_xyz('test.xyz',
    set_mol_name=['CaM_1', 'CaM_2'],
    read_model=[1, 5], set_model_num=[1,
    1])
```

To load the files ‘test_1.xyz’, ‘test_2.xyz’, ‘test_3.xyz’ and ‘test_4.xyz’ as models, type the following sequence of commands:

```
relax> structure.read_xyz('test_1.xyz',
    set_mol_name='test_1', set_model_num=1)
```

```
relax> structure.read_xyz('test_2.xyz',
    set_mol_name='test_2', set_model_num=2)
```

```
relax> structure.read_xyz('test_3.xyz',
    set_mol_name='test_3', set_model_num=3)
```

```
relax> structure.read_xyz('test_4.xyz',
    set_mol_name='test_4', set_model_num=4)
```

13.2.208 structure.rmsd**Synopsis**

Determine the RMSD between the models.

Defaults

```
structure.rmsd(atom_id=None)
```

Keyword arguments

atom_id: The atom identification string.

Description

This allows the root mean squared deviation (RMSD) between all models to be calculated.

The atom ID, which uses the same notation as the spin ID strings, can be used to restrict the RMSD calculation to certain molecules, residues, or atoms.

Prompt examples

To determine the RMSD, simply type:

```
relax> structure.rmsd()
```



13.2.209 structure.rotate



Synopsis

Rotate the internal structural object about the given origin by the rotation matrix.

Defaults

```
structure.rotate(R=array([[ 1., 0., 0.], [ 0., 1., 0.], [ 0., 0., 1.]]), origin=None, model=None, atom_id=None)
```

Keyword arguments

- R:** The rotation matrix in forwards rotation notation.
- origin:** The origin or pivot of the rotation.
- model:** The model to rotate (which if not set will cause all models to be rotated).
- atom_id:** The atom identification string.

Description

This is used to rotate the internal structural data by the given rotation matrix. If the origin is supplied, then this will act as the pivot of the rotation. Otherwise, all structural data will be rotated about the point [0, 0, 0]. The rotation can be restricted to one specific model.

13.2.210 structure.superimpose



Synopsis

Superimpose a set of models of the same structure.

Defaults

```
structure.superimpose(models=None, method='fit to mean', atom_id=None, centroid=None)
```

Keyword arguments

- models:** The list of models to superimpose.
- method:** The superimposition method.
- atom_id:** The atom identification string.
- centroid:** The alternative position of the centroid.

Description

This allows a set of models of the same structure to be superimposed to each other. Two superimposition methods are currently supported:

'fit to mean' – All models are fit to the mean structure. This is the default and most accurate method for an ensemble description. It is an iterative method which first calculates a mean structure and then fits each model to the mean structure using the Kabsch algorithm. This is repeated until convergence.

'fit to first' – This is quicker but is not as accurate for an ensemble description. The Kabsch algorithm is used to rotate and translate each model to be superimposed onto the first model.

If the list of models is not supplied, then all models will be superimposed.

The atom ID, which uses the same notation as the spin ID strings, can be used to restrict the superimpose calculation to certain molecules, residues, or atoms. For example to only superimpose backbone heavy atoms in a protein, use the atom ID of '`@N,C,CA,O`', assuming those are the names of the atoms from the structural file.

By supplying the position of the centroid, an alternative position than the standard rigid body centre is used as the focal point of the superimposition. The allows, for example, the superimposition about a pivot point.

Prompt examples

To superimpose all sets of models, type one of:

```
relax> structure.superimpose()
```

```
relax> structure.superimpose(method='fit to
mean')
```

To superimpose the models 1, 2, 3, 5 onto model 4, type:

```
relax> structure.superimpose(models=[4, 1,
2, 3, 5], method='fit to first')
```

To superimpose an ensemble of protein structures using only the backbone heavy atoms, type one of:

```
relax> structure.superimpose(atom_id='@N,C,
CA,O')
```

```
relax> structure.superimpose(method='fit to
mean', atom_id='@N,C,CA,O')
```

To superimpose model 2 onto model 3 using backbone heavy atoms, type one of:

```
relax> structure.superimpose([3, 2], 'fit to
first', '@N,C,CA,O')
```

```
relax> structure.superimpose(models=[3, 2],
method='fit to first', atom_id='@N,C,CA
,O')
```

13.2.211 structure.translate



Synopsis

Laterally displace the internal structural object by the translation vector.

Defaults

```
structure.translate(T=None, model=None, atom_id=
None)
```

Keyword arguments

T: The translation vector.

model: The model to translate (which if not set will cause all models to be translated).

atom_id: The atom identification string.

Description

This is used to translate the internal structural data by the given translation vector. The translation can be restricted to one specific model.

13.2.212 structure.web_of_motion**Synopsis**

Create a PDB representation of motion between models using a web of interconnecting lines.

Defaults

```
structure.web_of_motion(file=None, dir=None, models=None, force=False)
```

Keyword arguments

file: The name of the PDB file.

dir: The directory to save the file to.

models: Restrict the web to a subset of models.

force: A flag which if set to True will cause any pre-existing files to be overwritten.

Description

This will create a PDB representation of the motion between the atoms of a given set of structural models. Identical atoms of the selected models are concatenated into one model, within a temporary internal structural object, and linked together using PDB CONECT records.

Prompt examples

To create a web of motion for the models 1, 3, and 5, type one of:

```
relax> structure.web_of_motion('web.pdb', '.', [1, 3, 5])
```

```
relax> structure.web_of_motion(file='web.pdb  
', models=[1, 3, 5])
```

```
relax> structure.web_of_motion(file='web.pdb  
', dir='.', models=[1, 3, 5])
```

13.2.213 structure.write_pdb**Synopsis**

Writing structures to a PDB file.

**Defaults**

```
structure.write_pdb(file=None, dir=None, model_num=None, compress_type=0, force=False)
```

Keyword arguments

file: The name of the PDB file.

dir: The directory where the file is located.

model_num: Restrict the writing of structural data to a single model in the PDB file.

compress_type: The type of compression to use when creating the file.

force: A flag which if set to True will cause any pre-existing files to be overwritten.

Description

This will write all of the structural data loaded in the current data pipe to be converted to the PDB format and written to file. Specifying the model number allows single models to be output.

The default behaviour of this function is to not compress the file. The compression can, however, be changed to either bzip2 or gzip compression. If the '.bz2' or '.gz' extension is not included in the file name, it will be added. This behaviour is controlled by the compression type which can be set to

0 – No compression (no file extension).

1 – bzip2 compression ('.bz2' file extension).

2 – gzip compression ('.gz' file extension).

Prompt examples

To write all models and molecules to the PDB file ‘ensemble.pdb’ within the directory ‘~/pdb’, type one of:

```
relax> structure.write_pdb('ensemble.pdb', '  
~/pdb')
```

13.2.214 sys_info

```
relax> structure.write_pdb(file='  
ensemble.pdb', dir='pdb')
```

Synopsis

To write model number 3 into the new file ‘test.pdb’, use one of:

```
relax> structure.write_pdb('test.pdb',  
model_num=3)
```

Defaults

```
relax> structure.write_pdb(file='test.pdb',  
model_num=3)
```

`sys.info()`**Description**

This will display all of the relax, Python, python package and hardware information currently being used by relax. This is useful for seeing if all packages are up to date and if the correct software versions are being used. It is also very useful information for reporting relax bugs.

‘**x***’ – Match the character ‘x’ any number of times, for example ‘x’ will match, as will ‘xxxxx’.

‘**.***’ – Match any sequence of characters of any length.

13.2.215 value.copy



Synopsis

Copy spin specific data values from one data pipe to another.

Defaults

```
value.copy(pipe_from=None, pipe_to=None, param=None)
```

Keyword arguments

pipe_from: The name of the pipe to copy from.

pipe_to: The name of the pipe to copy to.

param: The parameter to copy. Only one parameter may be selected.

Description

If this is used to change values of previously minimised parameters, then the minimisation statistics (chi-squared value, iteration count, function count, gradient count, and Hessian count) will be reset.

Regular expression

The python function ‘`match`’, which uses regular expression, is used to determine which data type to set values to, therefore various `data_type` strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

‘**[]**’ – A sequence or set of characters to match to a single character. For example, ‘[ss]2’ will match both ‘S2’ and ‘s2’.

‘**^**’ – Match the start of the string.

‘**\$**’ – Match the end of the string. For example, ‘^ [Ss]2\$’ will match ‘s2’ but not ‘S2f’ or ‘s2s’.

‘**.**’ – Match any character.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Model-free set details

Setting a parameter value may have no effect depending on which model-free model is chosen, for example if S_f^2 values and S_s^2 values are set but the run corresponds to model-free model ‘m4’ then, because these data values are not parameters of the model, they will have no effect.

Note that the R_{ex} values are scaled quadratically with field strength and should be supplied as a field strength independent value. Use the following formula to get the correct value:

```
value = rex / (2.0 * pi * frequency) ** 2
```

where:

rex is the chemical exchange value for the current frequency.

π is in the namespace of relax, ie just type ‘ π ’.

frequency is the proton frequency corresponding to the data.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Reduced spectral density mapping set details

In reduced spectral density mapping, three values must be set prior to the calculation of spectral density values: the bond length, CSA, and heteronucleus type.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Consistency testing set details

In consistency testing, only four values can be set, the bond length, CSA, angle Theta ('orientation') and correlation time values. These must be set prior to the calculation of consistency functions.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

Relaxation curve fitting set details

Only three parameters can be set, the relaxation rate (R_x), the initial intensity (I_0), and the intensity at infinity (I_{∞}). Setting the parameter I_{∞} has no effect if the chosen model is that of the exponential curve which decays to zero.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

N-state model set details

Setting parameters for the N-state model is a little different from the other type of analyses as each state has a set of parameters with the same names as the other states. To set the parameters for a specific state c (ranging from 0 for the first to $N-1$ for the last, the number c should be added to the end of the parameter name. So the Euler angle γ of the third state is specified using the string 'gamma2'.

N-state model data type string matching patterns

Please see Table 13.23 on page 405.

The objects corresponding to the object names are lists (or arrays) with each element corresponding to each state.

Prompt examples

To copy the CSA values from the data pipe 'm1' to 'm2', type:

```
relax> value.copy('m1', 'm2', 'csa')
```

13.2.216 value.display

A°



Synopsis

Display spin specific data values.

Defaults

```
value.display(param=None, scaling=1.0)
```

Keyword arguments

param: The parameter to display. Only one parameter may be selected.

scaling: The factor to scale parameters by.

Description

The values corresponding to the given parameter will be displayed. The scaling argument can be used to scale the parameter values. This can be useful for example in the case of the model-free R_{ex} parameter to obtain the spectrometer dependent value from the omega_ex field strength independent internal value. Or to scale correlation times from seconds down to nanosecond or picosecond timescales.

Regular expression

The python function 'match', which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

'[]' – A sequence or set of characters to match to a single character. For example, '[sS]2' will match both 'S2' and 's2'.

'^' – Match the start of the string.

'\$' – Match the end of the string. For example, '^[\$s]2\$' will match 's2' but not 'S2f' or 's2s'.

'.' – Match any character.

Table 13.23: N-state model data type string matching patterns.

Data type	Object name	Patterns
Probabilities	'probs'	'p0', 'p1', 'p2', ..., 'pN'
Euler angle α	'alpha'	'alpha0', 'alpha1', ...
Euler angle β	'beta'	'beta0', 'beta1', ...
Euler angle γ	'gamma'	'gamma0', 'gamma1', ...
Bond length	'r'	'^r\$' or '[Bb]ond[-][Ll]ength'
Heteronucleus type	'heteronuc_type'	'[Hh]eteronucleus\$'
Proton type	'proton_type'	'[Pp]roton\$'

'x*' – Match the character 'x' any number of times, for example 'x' will match, as will 'xxxxx'.

'.*' – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Model-free parameter writing details

For the model-free theory, it is assumed that R_{ex} values are scaled quadratically with field strength. The values will seem quite small as they will be written out as a field strength independent value. Hence please use the following formula to convert the value to that expected for a given magnetic field strength:

```
Rex = value * (2.0 * pi * frequency) ** 2
```

The frequency is that of the proton in Hertz.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

NOE calculation data type string matching patterns

Please see Table 13.6 on page 272.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

N-state model data type string matching patterns

Please see Table 13.23 on page 405.

The objects corresponding to the object names are lists (or arrays) with each element corresponding to each state.

Prompt examples

To show all CSA values, type:

```
relax> value.display('csa')
```

To display the model-free R_{ex} values scaled to 600 MHz, type one of:

```
relax> value.display('rex', scaling=(2.0*pi
*600e6)**2)
```

```
relax> value.display(param='rex', scaling=(2
.0*pi*600e6)**2)
```

Description

13.2.217 value.read

Å



Synopsis

Read spin specific data values from a file.

Defaults

```
value.read(param=None, scaling=1.0, file=None, dir=
None, spin_id_col=None, mol_name_col=None,
res_num_col=None, res_name_col=None, spin_num_col=
None, spin_name_col=None, data_col=None, error_col=
None, sep=None, spin_id=None)
```

Keyword arguments

param: The parameter. Only one parameter may be selected.

scaling: The factor to scale parameters by.

file: The name of the file containing the values.

dir: The directory where the file is located.

spin_id_col: The spin ID string column (an alternative to the mol, res, and spin name and number columns).

mol_name_col: The molecule name column (alternative to the spin_id_col).

res_num_col: The residue number column (alternative to the spin_id_col).

res_name_col: The residue name column (alternative to the spin_id_col).

spin_num_col: The spin number column (alternative to the spin_id_col).

spin_name_col: The spin name column (alternative to the spin_id_col).

data_col: The RDC data column.

error_col: The experimental error column.

sep: The column separator (the default is white space).

spin_id: The spin ID string to restrict the loading of data to certain spin subsets.

The spin system can be identified in the file using two different formats. The first is the spin ID string column which can include the molecule name, the residue name and number, and the spin name and number. Alternatively the molecule name, residue number, residue name, spin number and/or spin name columns can be supplied allowing this information to be in separate columns. Note that the numbering of columns starts at one. The spin ID string can be used to restrict the reading to certain spin types, for example only ^{15}N spins when only residue information is in the file.

If this is used to change values of previously minimised parameters, then the minimisation statistics (chi-squared value, iteration count, function count, gradient count, and Hessian count) will be reset.

Regular expression

The python function ‘`match`’, which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

‘[]’ – A sequence or set of characters to match to a single character. For example, ‘[sS]2’ will match both ‘S2’ and ‘s2’.

‘^’ – Match the start of the string.

‘\$’ – Match the end of the string. For example, ‘^Ss2\$’ will match ‘s2’ but not ‘S2f’ or ‘s2s’.

‘.’ – Match any character.

‘x*’ – Match the character ‘x’ any number of times, for example ‘x’ will match, as will ‘xxxx’.

‘.*’ – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Model-free set details

Setting a parameter value may have no effect depending on which model-free model is chosen, for example if S_f^2 values and S_s^2 values are set but the run corresponds to model-free model ‘m4’ then, because these data values are not parameters of the model, they will have no effect.

Note that the R_{ex} values are scaled quadratically with field strength and should be supplied as a field strength independent value. Use the following formula to get the correct value:

`value = rex / (2.0 * pi * frequency) ** 2` **N-state model set details**

where:

`rex` is the chemical exchange value for the current frequency.

`π` is in the namespace of relax, ie just type ‘`π`’.

`frequency` is the proton frequency corresponding to the data.

Setting parameters for the N-state model is a little different from the other type of analyses as each state has a set of parameters with the same names as the other states. To set the parameters for a specific state `c` (ranging from 0 for the first to `N-1` for the last, the number `c` should be added to the end of the parameter name. So the Euler angle γ of the third state is specified using the string ‘`gamma2`’.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

N-state model data type string matching patterns

Please see Table 13.23 on page 405.

The objects corresponding to the object names are lists (or arrays) with each element corresponding to each state.

Reduced spectral density mapping set details

In reduced spectral density mapping, three values must be set prior to the calculation of spectral density values: the bond length, CSA, and heteronucleus type.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Prompt examples

To load 15N CSA values from the file ‘`csa_values`’ in the directory ‘`data`’, where spins are only identified by residue name and number, type one of the following:

```
relax> value.read('csa', 'data/csa_value',
    spin_id='@N')

relax> value.read('csa', 'csa_value', dir='
    data', spin_id='@N')

relax> value.read(param='csa', file='
    csa_value', dir='data', res_num_col=1,
    res_name_col=2, data_col=3, error_col
    =4, spin_id='@N')
```

Consistency testing set details

In consistency testing, only four values can be set, the bond length, CSA, angle Theta (‘`orientation`’) and correlation time values. These must be set prior to the calculation of consistency functions.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

Relaxation curve fitting set details

Only three parameters can be set, the relaxation rate (`Rx`), the initial intensity (`I0`), and the intensity at infinity (`Iinf`). Setting the parameter `Iinf` has no effect if the chosen model is that of the exponential curve which decays to zero.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

Regular expression

13.2.218 value.set

\AA

Synopsis

Set spin specific data values.

Defaults

`value.set(val=None, param=None, spin_id=None, error=False)`

Keyword arguments

val: The value(s).

param: The parameter(s).

spin_id: The spin ID string to restrict value setting to.

error: A flag which if True will cause the error rather than parameter to be set.

Description

If this function is used to change values of previously minimised results, then the minimisation statistics (chi-squared value, iteration count, function count, gradient count, and Hessian count) will be reset to None.

The value can be None, a single value, or an array of values while the parameter can be None, a string, or array of strings. The choice of which combination determines the behaviour of this function. The following table describes what occurs in each instance. In these columns, ‘None’ corresponds to None, ‘1’ corresponds to either a single value or single string, and ‘n’ corresponds to either an array of values or an array of strings.

Please see Table 13.24 on page 409.

Spin identification

If the spin ID is left unset, then this will be applied to all spins. If the data is global non-spin specific data, such as diffusion tensor parameters, supplying the spin identifier will terminate the program with an error.

The python function ‘`match`’, which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

‘[]’ – A sequence or set of characters to match to a single character. For example, ‘[sS]2’ will match both ‘S2’ and ‘s2’.

‘^’ – Match the start of the string.

‘\$’ – Match the end of the string. For example, ‘^ [Ss]2\$’ will match ‘s2’ but not ‘S2f’ or ‘s2s’.

‘.’ – Match any character.

‘x*’ – Match the character ‘x’ any number of times, for example ‘x’ will match, as will ‘xxxxx’.

‘.*’ – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Model-free set details

Setting a parameter value may have no effect depending on which model-free model is chosen, for example if S_f^2 values and S_s^2 values are set but the run corresponds to model-free model ‘m4’ then, because these data values are not parameters of the model, they will have no effect.

Note that the R_{ex} values are scaled quadratically with field strength and should be supplied as a field strength independent value. Use the following formula to get the correct value:

```
value = rex / (2.0 * pi * frequency) ** 2
```

where:

rex is the chemical exchange value for the current frequency.

π is in the namespace of relax, ie just type ‘ π ’.

frequency is the proton frequency corresponding to the data.

Table 13.24: The value and parameter combination options for the value.set user function.

Value	Param	Description
None	None	This case is used to set the model parameters prior to minimisation or calculation. The model parameters are set to the default values.
1	None	Invalid combination.
n	None	This case is used to set the model parameters prior to minimisation or calculation. The length of the val array must be equal to the number of model parameters. The parameters will be set to the corresponding number.
None	1	The parameter matching the string will be set to the default value.
1	1	The parameter matching the string will be set to the supplied number.
n	1	Invalid combination.
None	n	Each parameter matching the strings will be set to the default values.
1	n	Each parameter matching the strings will be set to the supplied number.
n	n	Each parameter matching the strings will be set to the corresponding number. Both arrays must be of equal length.

Table 13.25: Model-free default values.

Data type	Object name	Value
Local τ_m	'local_tm'	10 * 1e-9
Order parameters S^2 , S_f^2 , and S_s^2	's2', 's2f', 's2s'	0.8
Correlation time τ_e	'te'	100 * 1e-12
Correlation time τ_f	'tf'	10 * 1e-12
Correlation time τ_s	'ts'	1000 * 1e-12
Chemical exchange relaxation	'rex'	0.0
CSA	'csa'	-172 * 1e-6

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Model-free default values

Please see Table 13.25 on page 409.

Diffusion tensor set details

If the diffusion tensor has not been setup, use the more powerful function ‘`diffusion_tensor.init`’ to initialise the tensor parameters. This function cannot be used to initialise a diffusion tensor.

The units of the parameters are:

Inverse seconds for τ_m .

Seconds for \mathfrak{D}_{iso} , \mathfrak{D}_a , \mathfrak{D}_x , \mathfrak{D}_y , \mathfrak{D}_z , \mathfrak{D}_{\parallel} , \mathfrak{D}_{\perp} .

Unitless for \mathfrak{D}_{ratio} and \mathfrak{D}_r .

Radians for all angles (α , β , γ , θ , ϕ).

When setting a diffusion tensor parameter, the residue number has no effect. As the internal parameters of spherical diffusion are $\{\tau_m\}$, spheroidal diffusion are $\{\tau_m, \mathfrak{D}_a, \theta, \phi\}$, and ellipsoidal diffusion are $\{\tau_m, \mathfrak{D}_a, \mathfrak{D}_r, \alpha, \beta, \gamma\}$, supplying geometric parameters must be done in the following way. If a single geometric parameter is supplied, it must be one of τ_m , \mathfrak{D}_{iso} , \mathfrak{D}_a , \mathfrak{D}_r , or \mathfrak{D}_{ratio} . For the parameters \mathfrak{D}_{\parallel} , \mathfrak{D}_{\perp} , \mathfrak{D}_x , \mathfrak{D}_y , and \mathfrak{D}_z , it is not possible to determine how to use the currently set values together with the supplied value to calculate the new internal parameters. For spheroidal diffusion, when supplying multiple geometric parameters, the set must belong to one of

$\{\tau_m, \mathfrak{D}_a\}$,

$\{\mathfrak{D}_{iso}, \mathfrak{D}_a\}$,

$\{\tau_m, \mathfrak{D}_{ratio}\}$,

$\{\mathfrak{D}_{\parallel}, \mathfrak{D}_{\perp}\}$,

$\{\mathfrak{D}_{iso}, \mathfrak{D}_{ratio}\}$,

where either θ , ϕ , or both orientational parameters can be additionally supplied. For ellipsoidal diffusion, again when supplying multiple geometric parameters, the set must belong to one of

$\{\tau_m, \mathfrak{D}_a, \mathfrak{D}_r\}$,

$\{\mathfrak{D}_{iso}, \mathfrak{D}_a, \mathfrak{D}_r\}$,

$\{\mathfrak{D}_x, \mathfrak{D}_y, \mathfrak{D}_z\}$,

where any number of the orientational parameters, α , β , or γ can be additionally supplied.

Diffusion tensor parameter string matching patterns

Please see Table 13.3 on page 262.

Diffusion tensor parameter default values

Please see Table 13.26 on page 411.

Reduced spectral density mapping set details

In reduced spectral density mapping, three values must be set prior to the calculation of spectral density values: the bond length, CSA, and heteronucleus type.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Reduced spectral density mapping default values

These default values are found in the file ‘`physical_constants.py`’.

Please see Table 13.27 on page 411.

Consistency testing set details

In consistency testing, only four values can be set, the bond length, CSA, angle Theta (‘orientation’) and correlation time values. These must be set prior to the calculation of consistency functions.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

Consistency testing default values

These default values are found in the file ‘`physical_constants.py`’.

Please see Table 13.28 on page 411.

Table 13.26: Diffusion tensor parameter default values.

Data type	Object name	Value
tm	'tm'	10 * 1e-9
Diso	'Diso'	1.666 * 1e7
Da	'Da'	0.0
Dr	'Dr'	0.0
Dx	'Dx'	1.666 * 1e7
Dy	'Dy'	1.666 * 1e7
Dz	'Dz'	1.666 * 1e7
Dpar	'Dpar'	1.666 * 1e7
Dper	'Dper'	1.666 * 1e7
Dratio	'Dratio'	1.0
alpha	'alpha'	0.0
beta	'beta'	0.0
gamma	'gamma'	0.0
theta	'theta'	0.0
phi	'phi'	0.0

Table 13.27: Reduced spectral density mapping default values.

Data type	Object name	Value
CSA	'csa'	-172 * 1e-6

Table 13.28: Consistency testing default values.

Data type	Object name	Value
Bond length	'r'	1.02 * 1e-10
CSA	'csa'	-172 * 1e-6
Heteronucleus type	'heteronuc_type'	'15N'
Angle θ	'proton_type'	'1H'
Proton type	'orientation'	15.7
Correlation time	'tc'	13 * 1e-9

Relaxation curve fitting set details

Only three parameters can be set, the relaxation rate (R_x), the initial intensity (I_0), and the intensity at infinity (I_{∞}). Setting the parameter I_{∞} has no effect if the chosen model is that of the exponential curve which decays to zero.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

Relaxation curve fitting default values

These values are completely arbitrary as peak heights (or volumes) are extremely variable and the R_x value is a compensation for both the R_1 and R_2 values.

Please see Table 13.29 on page 413.

N-state model set details

Setting parameters for the N-state model is a little different from the other type of analyses as each state has a set of parameters with the same names as the other states. To set the parameters for a specific state c (ranging from 0 for the first to $N-1$ for the last, the number c should be added to the end of the parameter name. So the Euler angle γ of the third state is specified using the string ‘gamma2’.

N-state model data type string matching patterns

Please see Table 13.23 on page 405.

The objects corresponding to the object names are lists (or arrays) with each element corresponding to each state.

N-state model default values

Please see Table 13.30 on page 413.

In this table, N is the total number of states and c is the index of a given state ranging from 0 to $N-1$. The default probabilities are all set to be equal whereas the angles are given a range of values so that no 2 states are equal at the start of optimisation.

Note that setting the probability for state N will do nothing as it is equal to one minus all the other probabilities.

Prompt examples

To set the parameter values for the current data pipe to the default values, for all spins, type:

```
relax> value.set()
```

To set the parameter values of residue 10, which is in the current model-free data pipe ‘m4’ and has the parameters $\{S^2, \tau_e, R_{ex}\}$, the following can be used. R_{ex} term is the value for the first given field strength.

```
relax> value.set([0.97, 2.048*1e-9, 0.149], spin_id=':10')
```

```
relax> value.set(val=[0.97, 2.048*1e-9, 0.149], spin_id=':10')
```

To set the CSA value of all spins to the default value, type:

```
relax> value.set(param='csa')
```

To set the CSA value of all spins to -172 ppm, type:

```
relax> value.set(-172 * 1e-6, 'csa')
```

```
relax> value.set(val=-172 * 1e-6, param='csa')
```

To set the NH bond length of all spins to 1.02 Å, type:

```
relax> value.set(1.02 * 1e-10, 'r')
```

```
relax> value.set(val=1.02 * 1e-10, param='r')
```

To set both the bond length and the CSA value to the default values, type:

```
relax> value.set(param=['r', 'csa'])
```

To set both τ_f and τ_s to 100 ps, type:

```
relax> value.set(100e-12, ['tf', 'ts'])
```

```
relax> value.set(val=100e-12, param=['tf', 'ts'])
```

To set the S^2 and τ_e parameter values of residue 126, Ca spins to 0.56 and 13 ps, type:

```
relax> value.set([0.56, 13e-12], ['s2', 'te'], ':126@Ca')
```

```
relax> value.set(val=[0.56, 13e-12], param=['s2', 'te'], spin_id=':126@Ca')
```

```
relax> value.set(val=[0.56, 13e-12], param=['s2', 'te'], spin_id=':126@Ca')
```

Table 13.29: Relaxation curve fitting default values.

Data type	Object name	Value
Relaxation rate	'rx'	8.0
Initial intensity	'i0'	10000.0
Intensity at infinity	'iinf'	0.0

Table 13.30: N-state model default values.

Data type	Object name	Value
Probabilities	'p0', 'p1', 'p2', ..., 'pN'	1/N
Euler angle α	'alpha0', 'alpha1', ...	$(c+1) * \pi / (N+1)$
Euler angle β	'beta0', 'beta1', ...	$(c+1) * \pi / (N+1)$
Euler angle γ	'gamma0', 'gamma1', ...	$(c+1) * \pi / (N+1)$

13.2.219 value.write**Synopsis**

Write spin specific data values to a file.

Defaults

```
value.write(param=None, file=None, dir=None, scaling=1.0, comment=None, bc=False, force=False)
```

Keyword arguments

param: The parameter.

file: The name of the file.

dir: The directory name.

scaling: The factor to scale parameters by.

comment: Text which will be added to the start of the file as comments. All lines will be prefixed by '# '.

bc: A flag which if True will cause the back calculated values to be written to file rather than the actual data.

force: A flag which, if set to True, will cause the file to be overwritten.

Description

The values corresponding to the given parameter will be written to file. The scaling argument can be used to scale the parameter values. This can be useful for example in the case of the model-free R_{ex} parameter to obtain the spectrometer dependent value from the omega_ex field strength independent internal value. Or to scale correlation times from seconds down to nanosecond or picosecond timescales.

Regular expression

The python function ‘match’, which uses regular expression, is used to determine which data type to set values to, therefore various data_type strings can be used to select the same data type. Patterns used for matching for specific data types are listed below.

This is a short description of python regular expression, for more information see the regular expression syntax section of the Python Library Reference. Some of the regular expression syntax used in this function is:

‘[]’ – A sequence or set of characters to match to a single character. For example, ‘[sS]2’ will match both ‘S2’ and ‘s2’.

‘^’ – Match the start of the string.

‘\$’ – Match the end of the string. For example, ‘^Ss2\$’ will match ‘s2’ but not ‘S2f’ or ‘s2s’.

‘.’ – Match any character.

‘x*’ – Match the character ‘x’ any number of times, for example ‘x’ will match, as will ‘xxxx’.

‘.*’ – Match any sequence of characters of any length.

Importantly, do not supply a string for the data type containing regular expression. The regular expression is implemented so that various strings can be supplied which all match the same data type.

Model-free data type string matching patterns

Please see Table 13.4 on page 262.

Model-free parameter writing details

For the model-free theory, it is assumed that R_{ex} values are scaled quadratically with field strength. The values will seem quite small as they will be written out as a field strength independent value. Hence please use the following formula to convert the value to that expected for a given magnetic field strength:

```
Rex = value * (2.0 * pi * frequency) ** 2
```

The frequency is that of the proton in Hertz.

Reduced spectral density mapping data type string matching patterns

Please see Table 13.8 on page 272.

Consistency testing data type string matching patterns

Please see Table 13.9 on page 272.

NOE calculation data type string matching patterns

Please see Table 13.6 on page 272.

Relaxation curve fitting data type string matching patterns

Please see Table 13.7 on page 272.

N-state model data type string matching patterns

Please see Table 13.23 on page 405.

The objects corresponding to the object names are lists (or arrays) with each element corrsponding to each state.

Prompt examples

To write the CSA values to the file ‘csa.txt’, type one of:

```
relax> value.write('csa', 'csa.txt')
```

```
relax> value.write(param='csa', file='
    csa.txt')
```

To write the NOE values to the file ‘noe’, type one of:

```
relax> value.write('noe', 'noe.out')
```

```
relax> value.write(param='noe', file='
    noe.out')
```

```
relax> value.write(param='noe', file='
    noe.out')
```

```
relax> value.write(param='noe', file='
    noe.out', force=True)
```

To write the model-free R_{ex} values scaled to 600 MHz to the file ‘rex_600’, type one of:

```
relax> value.write('rex', 'rex_600', scaling
    =(2.0*pi*600e6)**2)
```

```
relax> value.write(param='rex', file='
    rex_600', scaling=(2.0*pi*600e6)**2)
```

13.2.220 vmd.view

Synopsis

View the structures loaded into the relax data store using VMD.

Defaults

vmd.view()

Description

This will launch VMD with all of the structures loaded into the relax data store.

Prompt examples

relax> vmd.view()

Chapter 14

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Version 3, 29 June 2007

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