

CalcALC User Manual

CalcALC is a Windows PC tool developed by Francis Pratt at ISIS for simulating and interpreting muon avoided level crossing (ALC) spectra of muoniated molecular radicals in both solid and liquid/gas phases using density functional theory (DFT).

It has two ways of working. It can either set up and automate Gaussian DFT calculations using the STFC SCARF compute cluster or it can take the output of previous independently made Gaussian or CASTEP magres calculations as the starting point for spectral simulation.

For the automatic mode, the starting point is a molecular structure defined in a file in pdb format. From this the user selects muon addition and substitution sites and a set of Gaussian jobs are prepared and submitted to the remote SCARF compute cluster which is operated by STFC Scientific Computing. Progress of the calculations is monitored and the completed DFT output files are returned to the host computer as the starting point for the spectral simulations.

From the single molecule Gaussian output files the program extracts muon and nuclear hyperfine parameters. It can also extract hyperfine parameters from CASTEP magres output files that may correspond to a periodic structure crystal calculation, such calculations have to be made independently before using CalcALC.

The radicals and strongly coupled nuclei contributing to the ALC spectrum are selected and used to build up the simulated spectrum using the Quantumtools python library developed by James Lord at ISIS.

The overall spectrum and its constituent components are finally plotted out using the GLE graphics layout engine.

Besides simulating the ALC spectra of open shell muon systems with finite hyperfine coupling, the program can also calculate electric field gradient tensors in closed shell diamagnetic muon systems and thus predict quadrupolar level crossing resonance (QLCR) spectra. Version 1.32 also now allows calculation of ZF/LF relaxation functions to be made in diamagnetic mode.

The CalcALC webpage is at: <https://shadow.nd.rl.ac.uk/calcalc/>

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What is needed to install and run CalcALC?

Windows

A windows machine or virtual machine is needed to run the software.

Python

A Python installation with the numpy module installed.

The windows path must include the location of python.exe and for python files which have the .py extension the default windows application must be set to python.exe.

Putty

For communicating with SCARF a full installation of [putty](#) is needed, giving the command line programs: putty.exe, plink.exe and pscp.exe. The windows path variable must include the location of these executables.

SCARF account

A SCARF account is needed for automatic calculation of hyperfine parameters of muon radical states using Gaussian DFT. Before using the CalcALC program test the SCARF account by using putty to log on to scarf.rl.ac.uk, saving the security key when prompted.

GLE4

The graphics package GLE4 is used to plot the polarisation spectra. This will be present on any system where the Wimda muon data analysis software has been fully installed or can be installed independently.

After these prerequisites have been checked and installed if necessary, the CalALC program can be installed.

CalcALC

The CalcALC installer program is CalcALCinstall.exe. After installation the PYTHONPATH environment variable should have been set to point to the location of the CalcALC installation folder.

Viewers for the pdb files are useful. Recommended are Jmol.jar as a simple java-based viewer and the CCDC viewer Mercury as a good full-featured option.

Running CalcALC

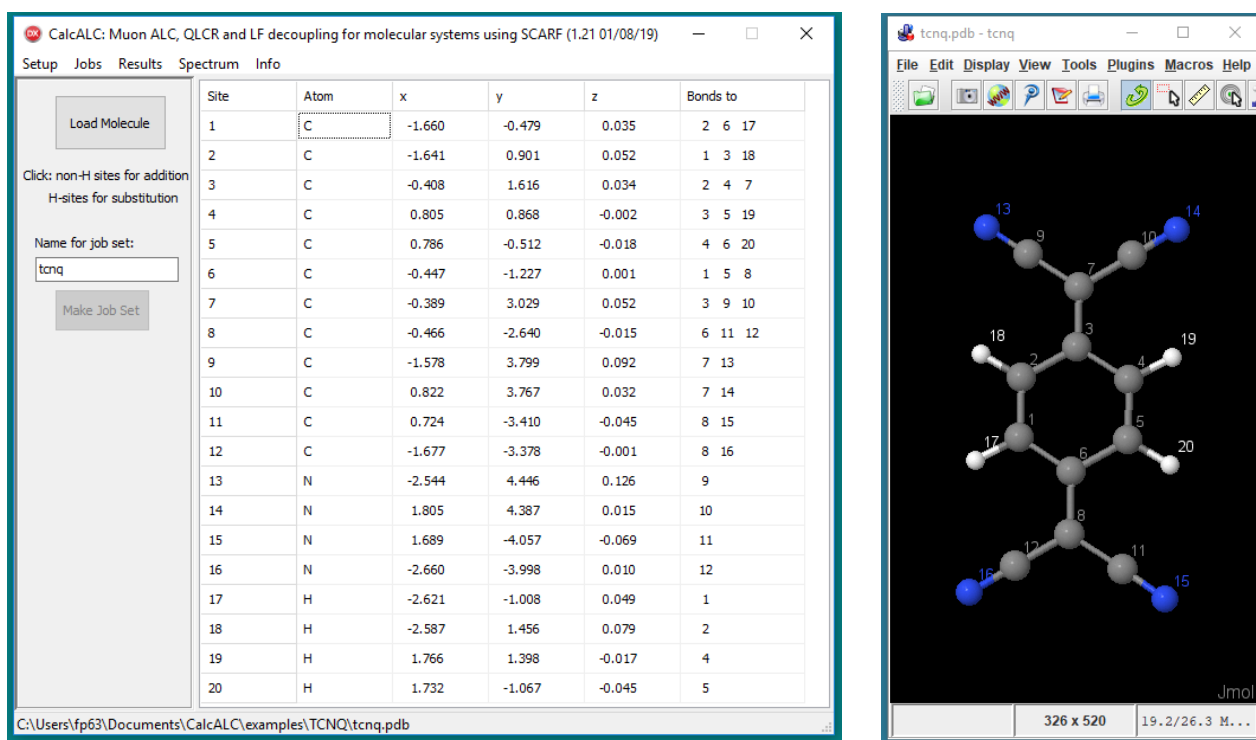
Step by step:

Step 1: Prepare the bare molecular structure in the form of pdb format file using suitable software (e.g. Mercury, Materials Studio, Crystalmaker etc.). A useful piece of software that allows conversion between structure formats is [openbabel](#).

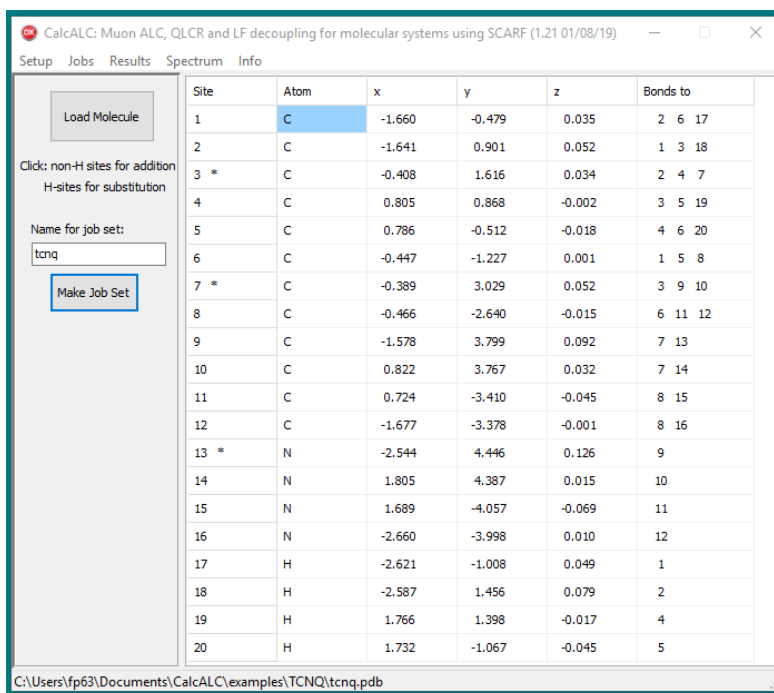
e.g. TCNQ

```
HETATM      1  C          1      -1.660  -0.479   0.035
HETATM      2  C          2      -1.641   0.901   0.052
HETATM      3  C          3      -0.408   1.616   0.034
HETATM      4  C          4       0.805   0.868  -0.002
HETATM      5  C          5       0.786  -0.512  -0.018
HETATM      6  C          6     -0.447  -1.227   0.001
HETATM      7  C          7     -0.389   3.029   0.052
HETATM      8  C          8     -0.466  -2.640  -0.015
HETATM      9  C          9     -1.578   3.799   0.092
HETATM     10  C         10       0.822   3.767   0.032
HETATM     11  C         11       0.724  -3.410  -0.045
HETATM     12  C         12     -1.677  -3.378  -0.001
HETATM     13  N         13     -2.544   4.446   0.126
HETATM     14  N         14       1.805   4.387   0.015
HETATM     15  N         15       1.689  -4.057  -0.069
HETATM     16  N         16     -2.660  -3.998   0.010
HETATM     17  H         17     -2.621  -1.008   0.049
HETATM     18  H         18     -2.587   1.456   0.079
HETATM     19  H         19       1.766   1.398  -0.017
HETATM     20  H         20       1.732  -1.067  -0.045
CONNECT      1      2      6      17
CONNECT      2      1      3      18
CONNECT      3      2      4       7
CONNECT      4      3      5      19
CONNECT      5      4      6      20
CONNECT      6      1      5       8
CONNECT      7      3      9      10
CONNECT      8      6     11      12
CONNECT      9      7     13
CONNECT     10      7     14
CONNECT     11      8     15
CONNECT     12      8     16
CONNECT     13      9
CONNECT     14     10
CONNECT     15     11
CONNECT     16     12
CONNECT     17      1
CONNECT     18      2
CONNECT     19      4
CONNECT     20      5
END
```

Step 2: Use the 'Load Molecule' button in the main CalcALC window to load in the pdb file. A viewer such as Jmol.jar or Mercury can be used to view the site numbering.



Click on the addition sites to include, each one selected will be marked by a *



Clicking on an H site marks it as a muon site (substitution site). This also provides a way of marking the muon site if a muon has already been included in the molecular structure file.

Step 3: Use the setup window to define the type of calculation. Pre-optimisation of the structure with semi-empirical methods before a single point DFT calculation provides an efficient and acceptably accurate calculation method. Full structural optimisation with DFT is also available as a much slower option.

Setup DFT

DFT Method: B3LYP

Basis set: cc-pVDZ

☒ Gaussian 16 ☐ Gaussian 09

Semi-empirical Pre-optimisation

☒ Pre-optimise

☒ PM3(M) ☐ PM3 ☐ PM6

☐ PM7(M) ☐ PM7

☐ Optimise structure with DFT

☐ Calculate EFG

☐ Reference state without the muon

Spin state: doublet

Charge state: 0

SCARF gateway: ui3.scarf.rl.ac.uk

SCARF username: fp63

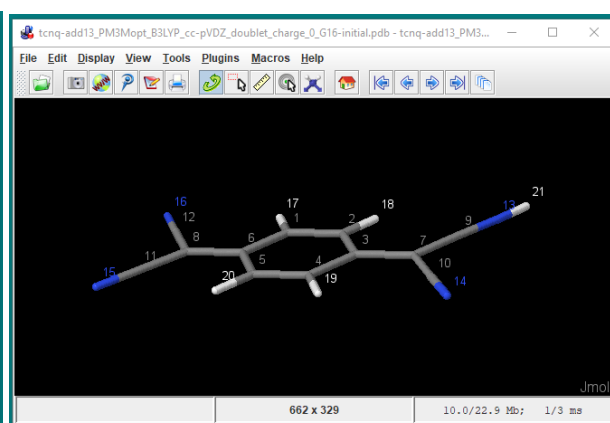
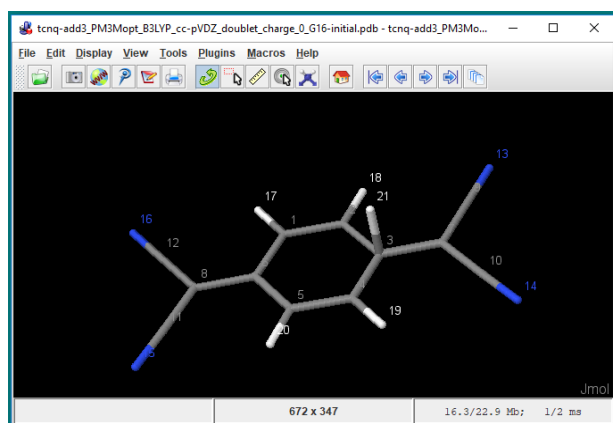
Cores: 4 Max hours: 4

When ready click the 'Make Job Set' button in the main CalCALC window which will insert entries in the jobs list window.

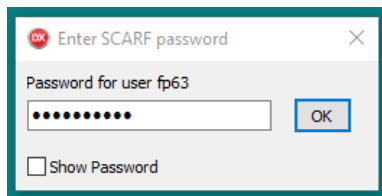
JOB-ID	STATUS	EXEC-HOST	JOB-NAME	SUBMIT-TIME	RUN-TIME
	MADE		tcnq-add3_PM3Mopt_B3LYP_cc-pVDZ_doublet_charge_0_G16		
	MADE		tcnq-add7_PM3Mopt_B3LYP_cc-pVDZ_doublet_charge_0_G16		
	MADE		tcnq-add13_PM3Mopt_B3LYP_cc-pVDZ_doublet_charge_0_G16		

Submit Jobs to SCARF Clear non-running jobs Remove Completed Jobs from List Kill All Submitted Jobs Job polling: ☐ Restart Polling

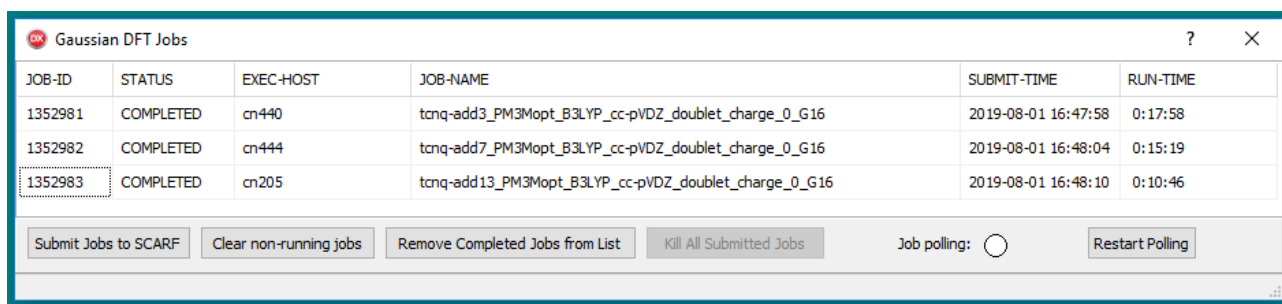
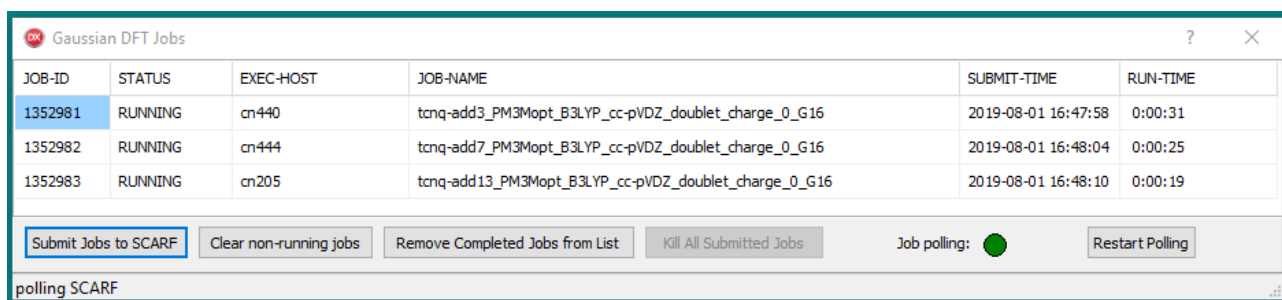
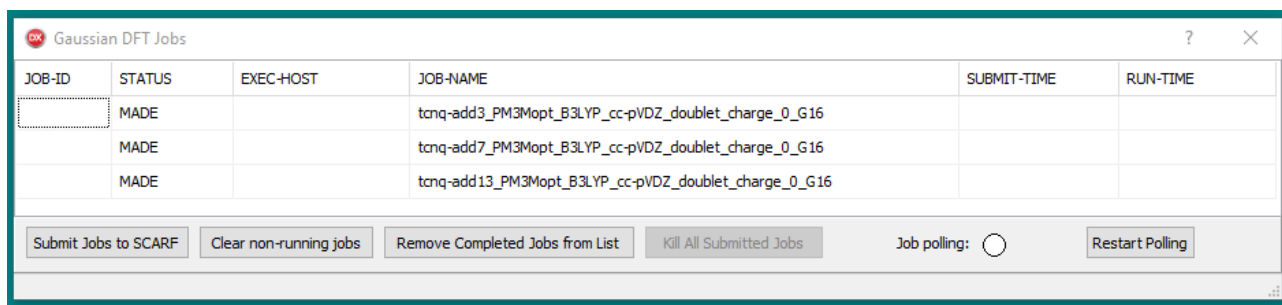
A viewer such as jmol.jar can be used to view and check the initial structure used for the radical.



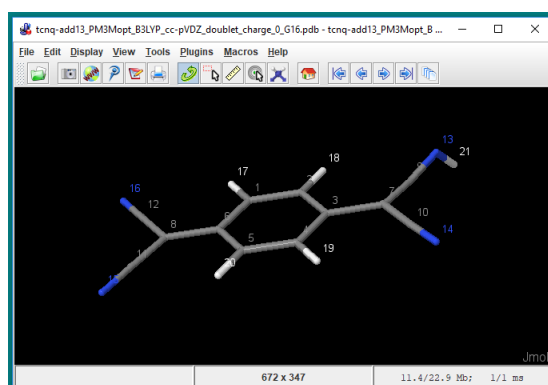
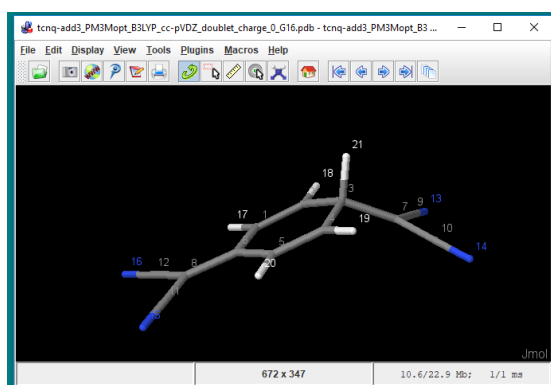
Step 4: The job set is submitted to SCARF from the Jobs window. A password will need to be supplied once within a session.



The set of jobs will be sent to SCARF and submitted to the queue and will start to run. The status of the jobs will be polled as they run.



When each job is completed the results file JOB-NAME.out will be copied back to the working directory on the user pc. After a certain time, all of the jobs will have finished (or failed). If a job fails, an editor such as Notepad++ can be used to explore the output file and determine the problem. The final structures of the successful jobs JOB-NAME.pdb can again be viewed with jmol.jar.



Step 5: The hyperfine parameters from the completed jobs are loaded into the results window and contributions to the ALC spectrum are selected and sent to the spectrum table to build up the spectrum. The muon and nuclei with spin are listed in the window.

Hyperfine Parameters from the DFT Output

Load DFT output

Muon site: 21

Energy (eV): -18482.270

Set E0

Click on atoms to include nuclei in spectrum

Show deuteration

Include minor isotopes

H:Mu prescaled

Nuclear grouping

Muon Site Quantum/Calibration/Thermal Factors

A 1.230 D1 1.000 D2 1.000 ☒ Auto

Global Nuclear Thermal/Calibration Factors

A 1.000 D1 1.000 D2 1.000

Single Site Nuclear Quantum Factors

A 1.000 D1 1.000 D2 1.000 Site 1

Full HFC Tensor

84.32 6.70 -3.76

6.70 87.88 -5.15

-3.76 -5.15 85.53

Axes

Major: 0.779 -0.625 -0.045

Mid : 0.341 0.363 0.867

Minor: 0.526 0.691 -0.496

Site number	Atom	Spin density	A (MHz)	D1 (MHz)	D2 (MHz)	DeltaM=1 (G)	DeltaM=0 (G)	Liquid FWHM (G)	Decoupling (G)	NQCC (MHz)	η
16	N	0.20949	9.4	15.9	2.3		2869	15.2	3.4		
15	N	0.20930	9.4	15.9	2.3		2870	15.2	3.4		
13	N	0.02640	6.8	3.1	0.3		2970	13.2	2.4		
21	Mu	0.00811	85.9	10.8	2.7	3154			30.7		
14	N	-0.00586	-0.3	-0.4	0.2		3238	10.9	0.1		
19	H	0.00292	4.4	2.4	0.8		4368	15.8	1.6		
18	H	0.00295	4.3	2.9	0.9		4372	15.8	1.5		
17	H	-0.00639	-10.2	5.8	2.0		5154	16.8	3.6		
20	H	-0.00690	-11.0	6.4	2.5		5198	17.0	3.9		

Add radical to ALC spectrum table

C:\Users\fp63\Documents\CalcALC\examples\TCNQ\tcnq-add13_PM3Mopt_B3LYP_cc-pVDZ_doublet_charge_0_G16.out

Clicking ‘Add radical to ALC Spectrum Table’ adds the muon on its own to the spectrum producing a Δ_1 resonance.

Table of Radicals Contributing to the ALC Spectrum

Radical #	Label	Mu/nucleus	Site number	A-bare	A-factor	A	D1-bare	D1-factor	D1	D2-bare	D2-factor	D2	Weighting
1		Mu	21	69.84	1.230	85.9	10.80	1.000	10.8	2.70	1.000	2.7	1.000

Clear Table

Remove Last Entry

Enter HFC manually

Global Factors

A-Mu 1.000 D1-Mu 1.000 D2-Mu 1.000

A-nuc 1.000 D1-nuc 1.000 D2-nuc 1.000

☐ Resonance set of a single radical

If one or more nuclei are clicked before adding the radical then the multispin system will show Δ_0 resonances as well.

Table of Radicals Contributing to the ALC Spectrum

Radical #	Label	Mu/nucleus	Site number	A-bare	A-factor	A	D1-bare	D1-factor	D1	D2-bare	D2-factor	D2	Weighting
1		Mu	21	69.84	1.230	85.9	10.80	1.000	10.8	2.70	1.000	2.7	1.000
		N	16	9.40	1.00	9.4	15.90	1.00	15.9	2.30	1.00	2.3	
		N	15	9.40	1.00	9.4	15.90	1.00	15.9	2.30	1.00	2.3	
		N	13	6.80	1.00	6.8	3.10	1.00	3.1	0.30	1.00	0.3	

Clear Table

Remove Last Entry

Enter HFC manually

Global Factors

A-Mu 1.000 D1-Mu 1.000 D2-Mu 1.000

A-nuc 1.000 D1-nuc 1.000 D2-nuc 1.000

☐ Resonance set of a single radical

Step 6: Parameters are set up for calculating and plotting the spectrum and the plot is generated

Solid state:

ALC Spectrum Generation

Field Range and Steps

Bmin: 1
Bmax: 10000
steps: 200
☐ Lin ☒ Log

Broadening

☒ no broadening
% ☐
G ☐ 2

Time Range (microseconds)

From: 0.00 To: 8.00

☐ Show combined spectrum

Plot name: TCNQ-N-site

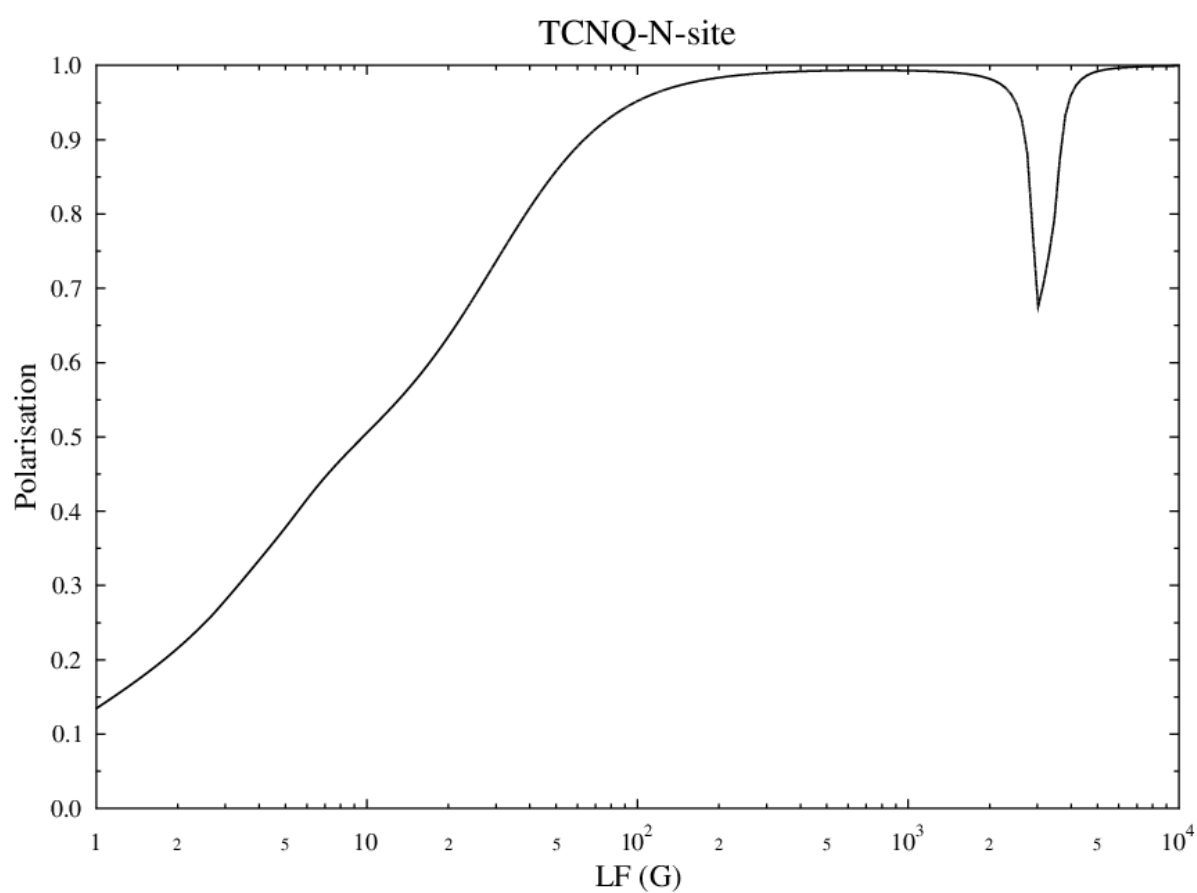
Generate Plot

Oriental averaging steps

100

Fast rotation about a single axis

Axis: 0 0 1 ☐ On



Liquid state just including Δ_0 resonances with the nitrogens:

ALC Spectrum Generation

Field Range and Steps

Bmin: 2500
Bmax: 3500
Bstep: 4

☒ Lin
☐ Log

Broadening

☒ no broadening
%
G

☐ Solid ☒ Liquid

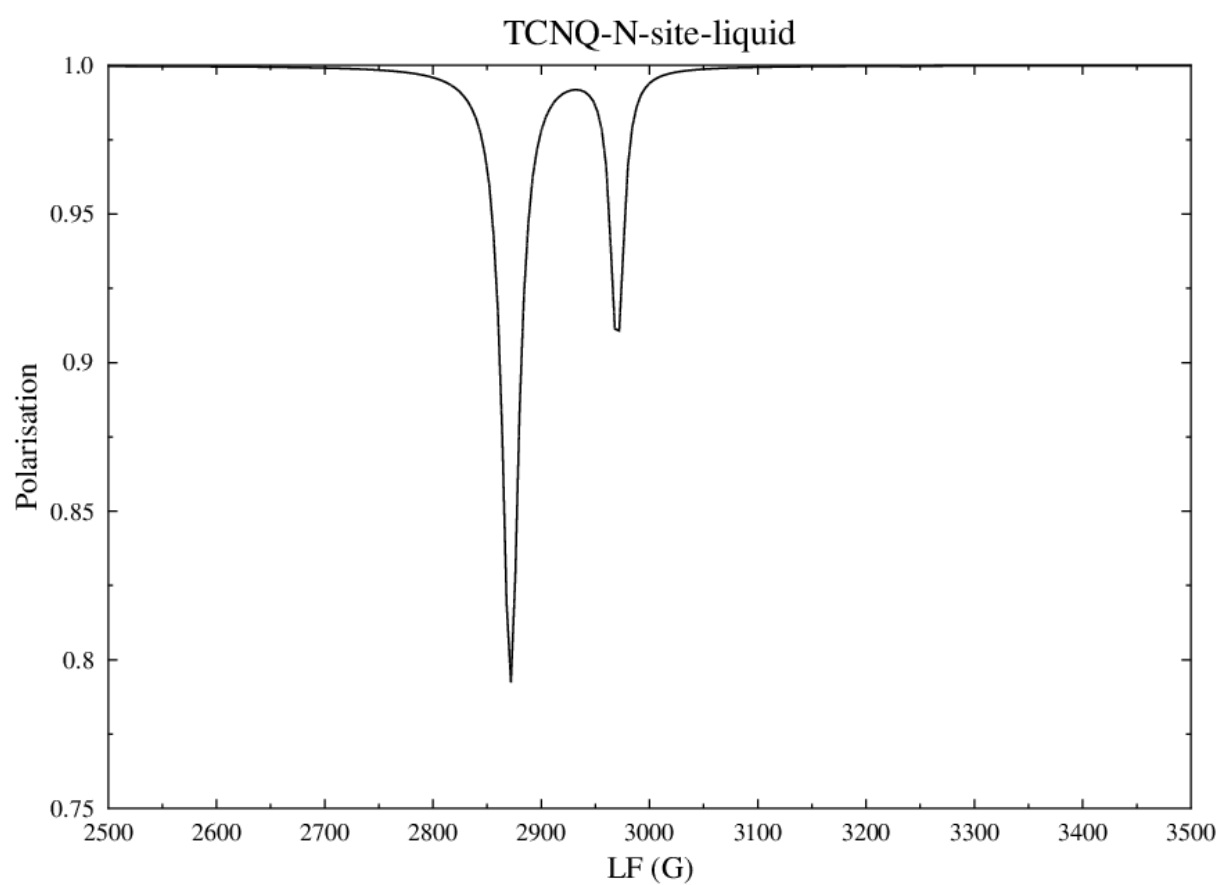
Time Range (microseconds)

From: 0.00 To: 8.00

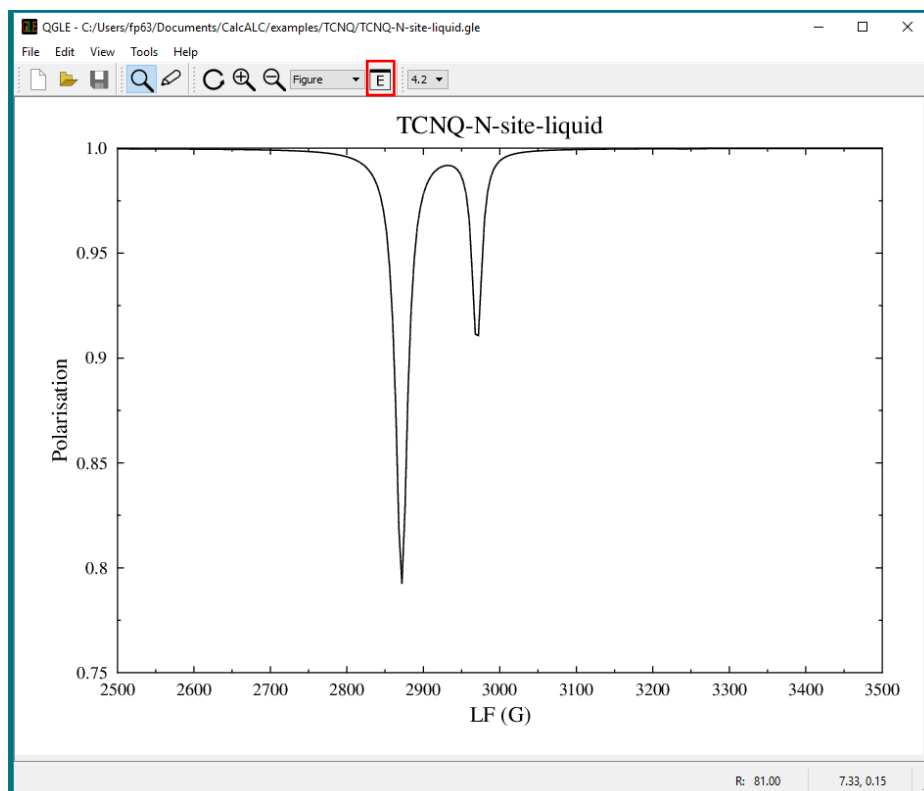
☐ Show combined spectrum

Plot name: TCNQ-N-site-liquid

Generate Plot



Step 7: Fine tuning of the plot by editing the gle plot definition file. The gle file can be edited in a text editor such as notepad++ to alter titles, axis labels, axis scaling etc. The E button on the top of the QGLE window can be set up to link directly to the editor for convenience.



```

C:\Users\fp63\Documents\CalcALC\examples\TCNQ\TCNQ-N-site-liquid.gle - Notepad++
File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ? X
TCNQ-N-site-liquid.gle
1 size 29 21
2 set font rm
3 hh=0.7
4 ht=0.7
5 set hei ht
6 set lwidth 0.03
7 lw=0.04
8 xmin=2500.00
9 xmax=3500.00
10 amove -2 -1
11 begin graph
12 size 35 24
13 title "TCNQ-N-site-liquid"
14 xtitle "LF (G)"
15 ytitle "Polarisation"
16 xaxis min xmin max xmax hei hh
17 xticks length tt
18 yaxis hei hh
19 xticks length tt
20 data "TCNQ-N-site-liquid-rad1.tab"
21 d1 smooth lstyle 1 lwidth lw color black
22 end graph
23
length: 380 lines: 23 Ln: 1 Col: 1 Sel: 0|0 Windows (CR LF) UTF-8 INS

```

This provides a quick guide to the basic operation of CalcALC. Some additional features of CalcALC are introduced in the various examples provided in the \examples folder.