

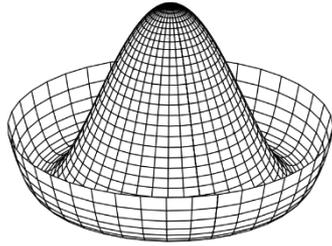
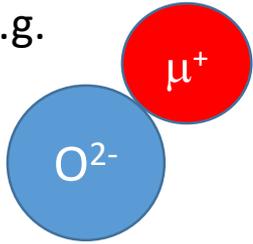


CalcALC: a User Tool for Predicting and Interpreting ALC and QLCR Spectra

Francis Pratt
ISIS Muon Group

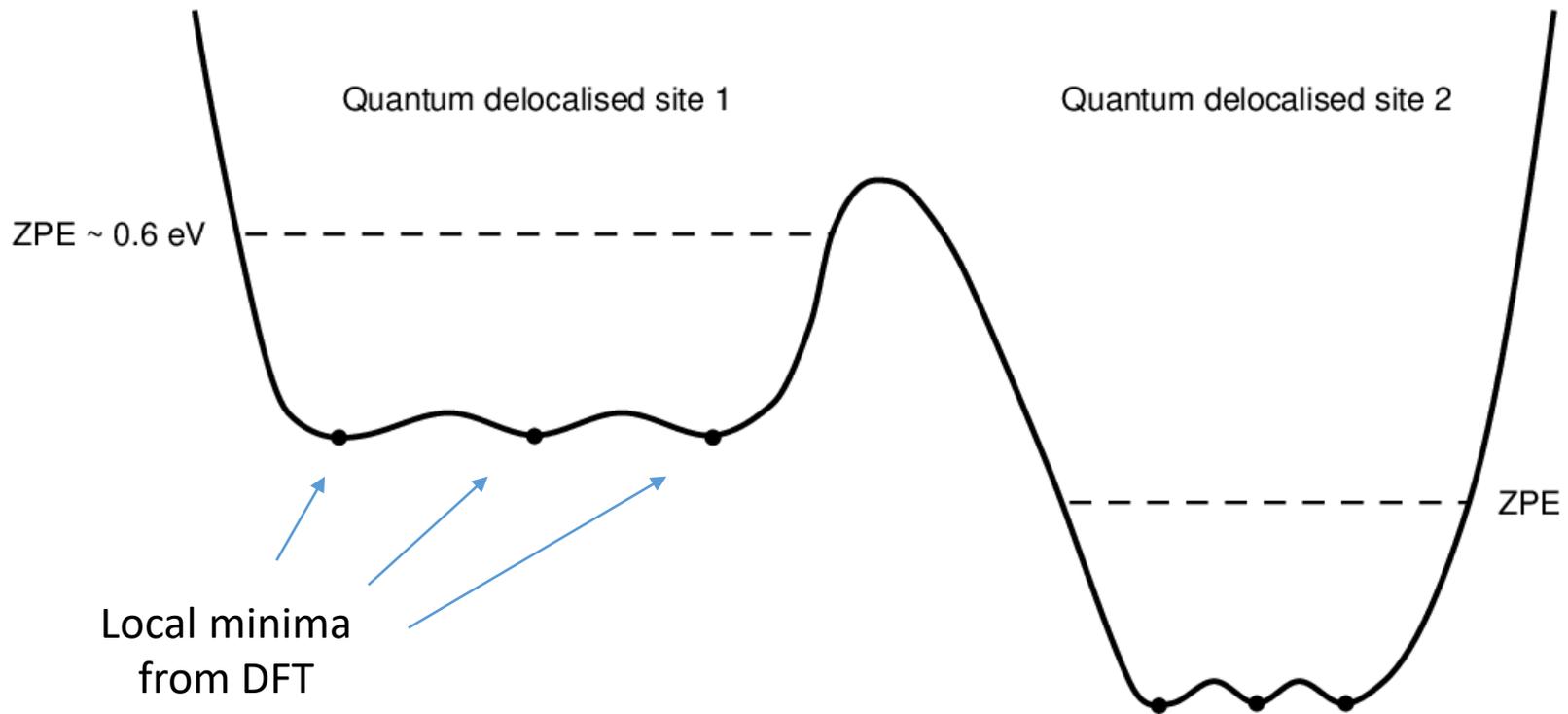
Energy Landscape and Quantum Effects

e.g.



Zero-point-energy (ZPE) dominated by stretch mode and the quantum correction factor (QF) for A is typically +20%

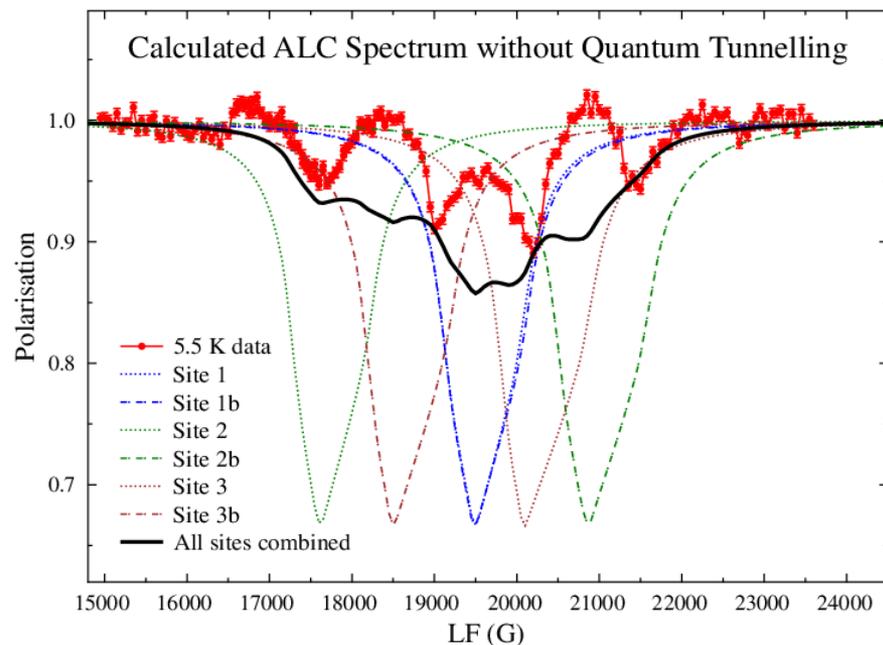
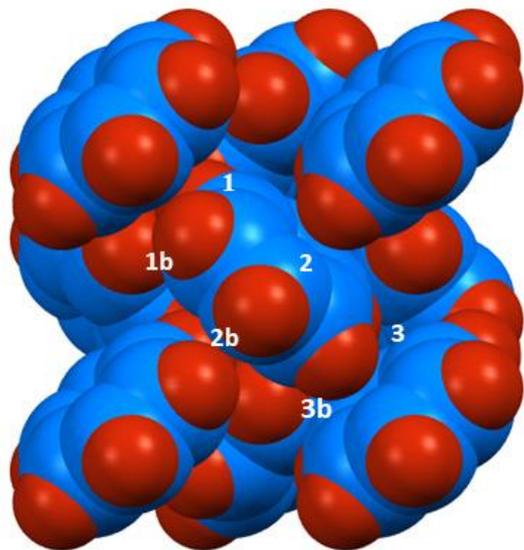
Rotation modes may also shift A significantly, e.g. the QF is found to be -150% for muoniated acetone $(CH_3)_2CO-Mu$



Example of ALC in Solid Benzene

CASTEP plane-wave DFT (SCD) gives six distinct sites and their associated hyperfine tensors

CalcALC simulates the corresponding ALC spectra

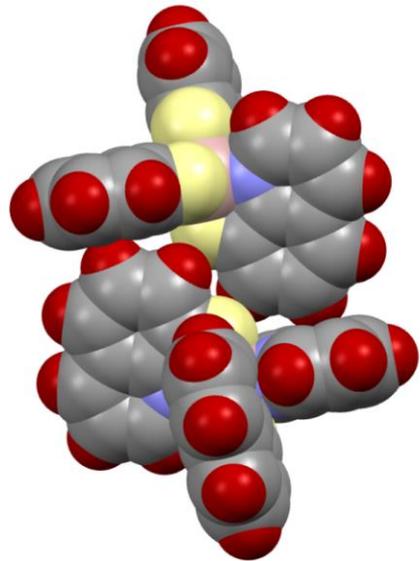
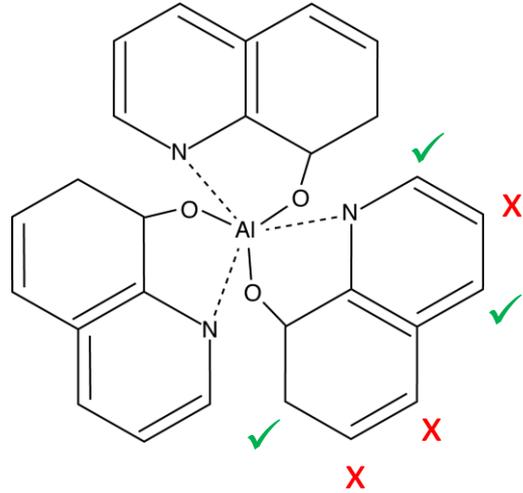


Quantum tunnelling of radical states is needed to describe the ALC spectra at low temperatures

The resonances reflect both intra-molecular tunnelling and inter-molecular tunnelling

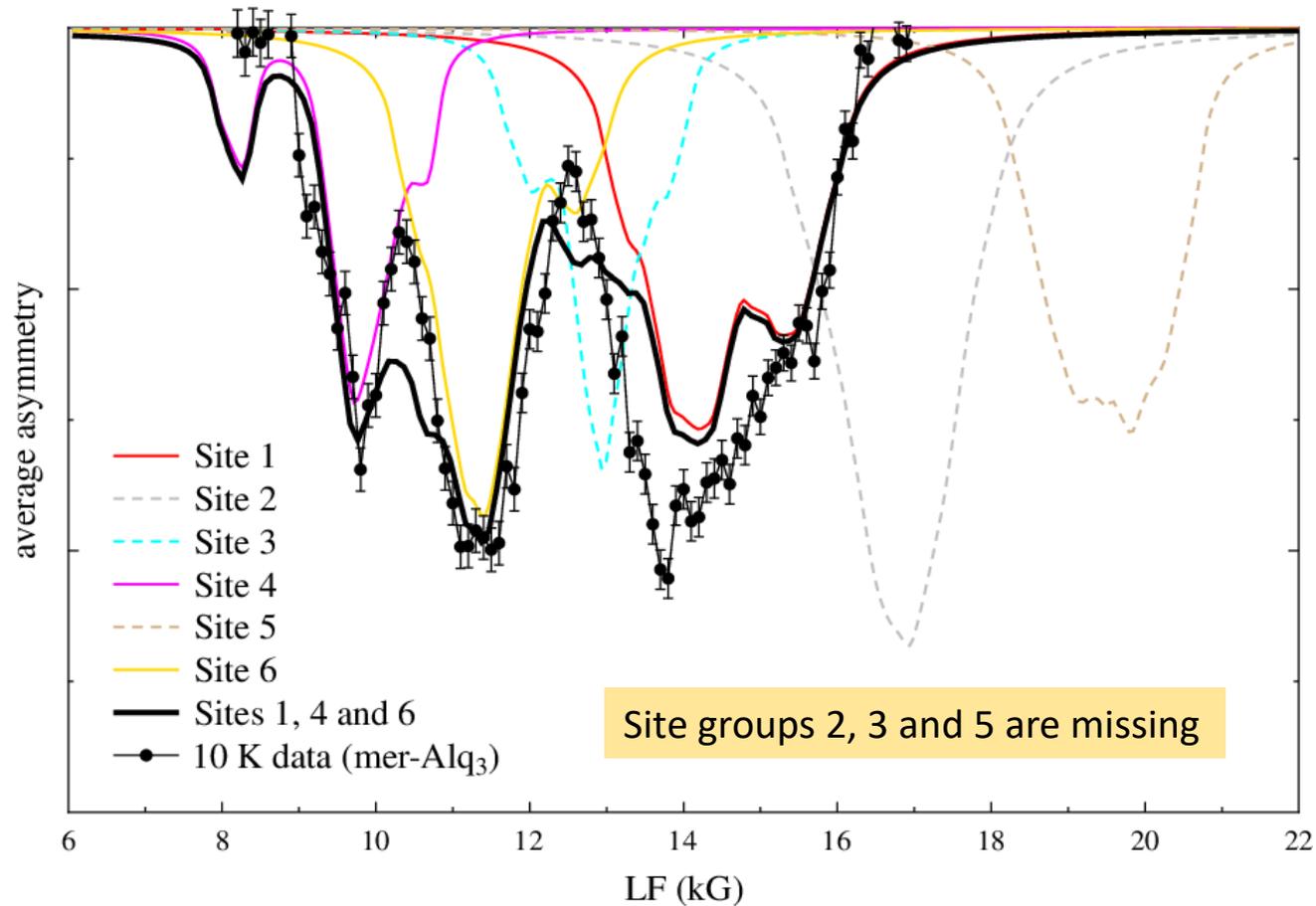
An entangled state of the muon, the electron and two protons is involved in the tunnelling

A more Complicated Molecule: Alq3

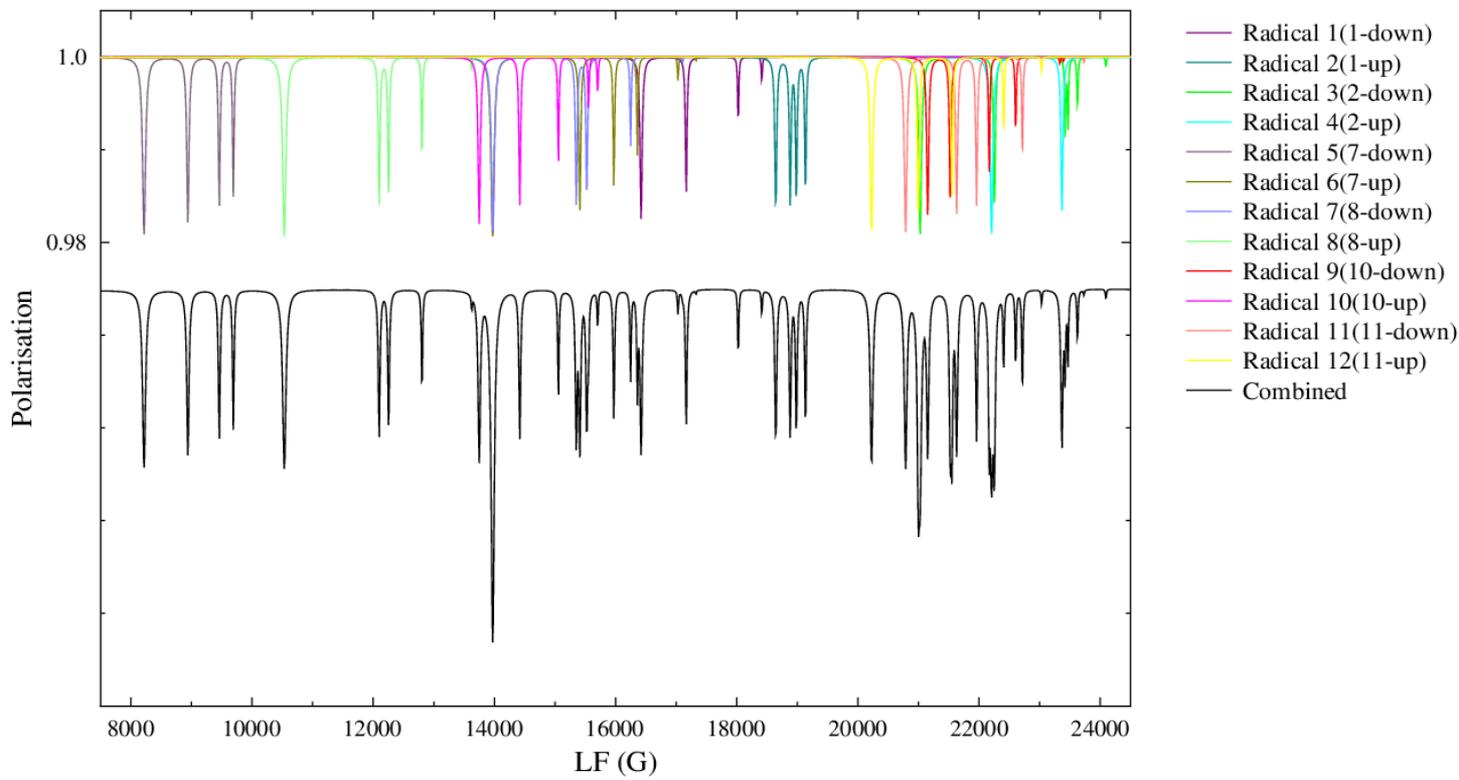
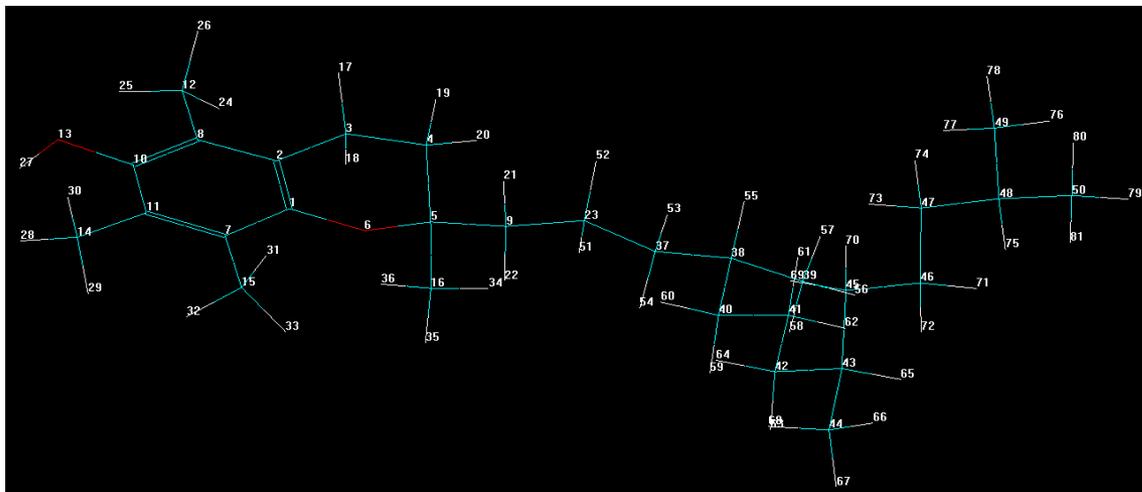


At least 36 distinct sites are possible

DFT Predicted Powder ALC Spectra for 36 Radicals in mer-Alq₃ (QF=1.11)



Even more complex: Δ_0 ALC Spectrum for Vitamin E



Diamagnetic Muon States: QLCR

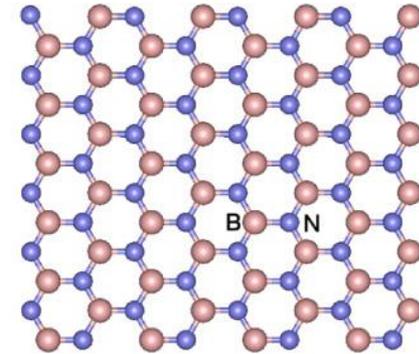
QLCR is a cross-relaxation between:

Muon Zeeman Splitting and Nuclear quadrupole splitting

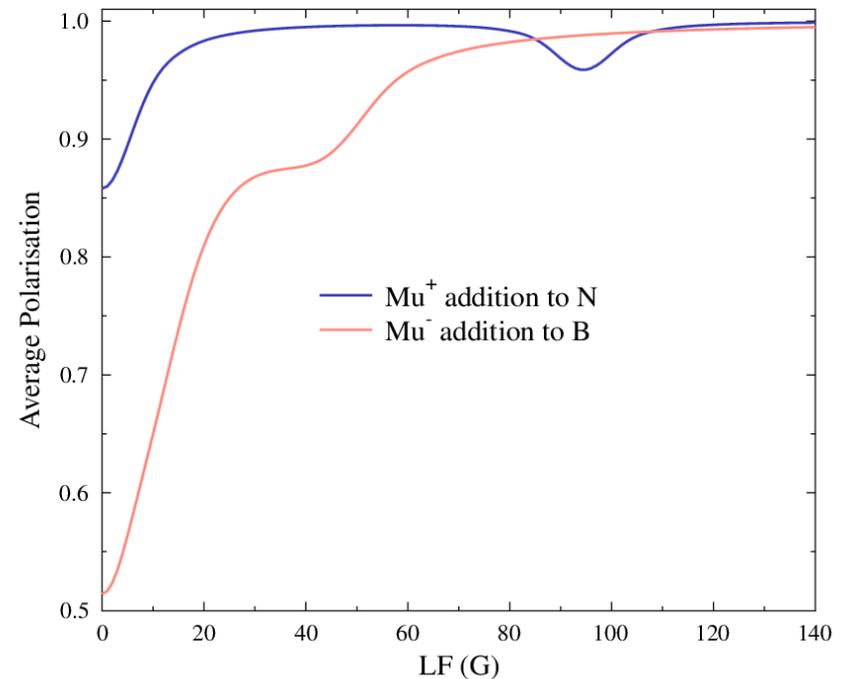
Quadrupole splittings depend on:

Nuclear spin (I)
Nuclear quadrupole moment (Q)
Electric field gradient (EFG) - *DFT*

Hexagonal BN



DFT Predicted QLCR for Hexagonal BN



CalcALC: Capabilities and Requirements

Capabilities:

Simulating and interpreting ALC and QLCR spectra in both solid and liquid/gas phases using density functional theory (DFT). The steps involved are:

- 1) Input molecular structure from a file in pdb format
- 2) Selection of muon addition or substitution sites, DFT method, charge, spin states etc.
- 3) Preparation of a set of Gaussian09 jobs for different sites
- 4) Job submission to SCARF, monitoring of progress and return of output files
- 5) Hyperfine and quadrupolar parameters extracted from output (CASTEP Magres also)
- 6) Spectra defined and calculated using the Quantumtools python libraries (James Lord)
- 7) Results plotted out using the GLE graphics layout engine

Requirements:

- 1) A Windows PC or a Windows virtual machine
- 2) A user account on the STFC compute cluster SCARF
- 3) Scp and ssh functions provided by the Putty package
- 4) Python 2.7 as provided by a Mantid installation for running Quantum
- 5) GLE as included in a WiMDA installation for plotting the spectra

CalcALC: From Molecule to ALC Spectrum via DFT

CalcALC: Muon ALC and LF decoupling for molecular radicals using Gaussian 09 on SCARF

Setup Jobs Results Spectrum

Load Molecule

Name for job set: benzene

Make Job Set

Site	Atom	x	y	z	Bonds to
1 *	C	0.793	0.560	-0.436	2 6 12
2	C	-0.342	1.245	-0.015	1 3 7
3	C	-1.476	0.540	0.373	2 4 8
4	C	-1.474	-0.851	0.343	3 5 9
5	C	-0.338	-1.536	-0.076	4 6 10
6	C	0.795	-0.831	-0.466	1 5 11
7	H	-0.343	2.339	0.010	2
8	H	-2.370	1.079	0.703	3
9	H	-2.367	-1.407	0.648	4
10	H	-0.336	-2.631	-0.097	5
11	H	1.689	-1.370	-0.798	6
12	H	1.685	1.116	-0.743	1

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\benzene\benzene.pdb

Setup DFT

DFT Method: B3LYP

Basis set: cc-pVDZ

Pre-optimize structure with PM3
 Pre-optimize structure with PM6
 Optimize structure with DFT

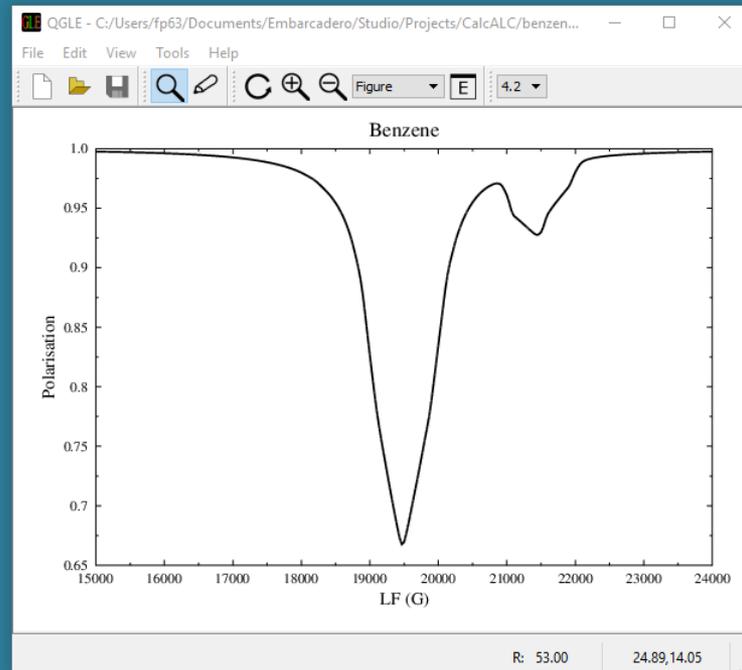
Spin state: doublet

Charge state: 0

SCARF username: fp63

Processor cores: 4

Max run time (hours): 4



Gaussian DFT Jobs

JOB-ID	STATUS	EXEC-HOST	JOB-NAME	SUBMIT-TIME	RUN-TIME
9955	DONE	4*cn063.scarf.rl.ac.uk	benzene-add1_PM3opt_B3LYP_cc-pVDZ_doublet_charge_0	08:36	0:01:50

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

Hyperfine Parameters from the DFT Output

Load DFT output

Energy (eV): -6334.965 Set E0

Click on atoms to select DeltaM=0 nuclei to include Include minor isotopes

Muon site: 13

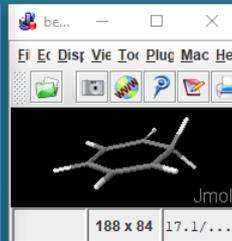
Muon Site Quantum/Calibration Factors: A 1.230 D1 1.000 D2 1.000 Auto

Nuclear Site Quantum/Calibration Factors: A 0.96 D1 1.000 D2 1.000

Site number	Atom	Spin density	A (MHz)	D1 (MHz)	D2 (MHz)	DeltaM=1 (G)	DeltaM=0 (G)	Liquid FWHM (G)	Decoupling (G)
13	Mu	0.06256	530.7	12.8	12.1	19484			189.4
12	H	0.06207	129.2	4.0	3.8		21479	122.9	46.1
10	H	0.00704	9.1	5.1	2.4		27959	16.8	3.2
8	H	0.00704	9.1	5.1	2.4		27959	16.8	3.2
7	H	-0.01857	-25.7	17.6	14.6		29838	23.4	9.2
11	H	-0.01857	-25.7	17.6	14.6		29838	23.4	9.2
9	H	-0.02403	-32.3	21.0	20.3		30197	26.7	11.5

Add radical to ALC spectrum table

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\benzene\benzene-add1_PM3opt_B3LYP_cc-pVDZ_doublet_charge_0.out



ALC Spectrum Generation

Field Range and Steps: Bmin 15000 Bmax 24000 Bstep 100 Lin Log

Broadening: 2 % 50 G no broadening

Time Range (microseconds): From 0.00 To 8.00

Plot name: Benzene

Generate Plot

Oriental averaging steps: 200 Solid State Liquid State

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	13	431.46	1.230	530.7	12.80	1.000	12.8	12.10	1.000	12.1	1.000
		H	12	134.58	0.96	129.2	4.00	1.000	4.0	3.80	1.000	3.8	

Global Factors

A-Mu 1.000 D1-Mu 1.000 D2-Mu 1.000 Resonance set of single radical

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

Clear Table

Input Structure Files

Require structure in pdb format with HETATM or ATOM entries specifying absolute atom positions and CONECT entries specifying their connectivity

The OpenBabel utility is available to convert from other structure formats

The image shows two windows from the CalcALC software. The left window displays a table of atom coordinates and the right window displays a PDB file for benzene.

CalcALC: Muon ALC, QLCR and LF decoupling for molecular systems using SCARF (v1.01)

Setup Jobs Results Spectrum

Load Molecule

Click: non-H sites for addition
H-sites for substitution

Name for job set:
benzene

Make Job Set

Site	Atom	x	y	z	Bonds to
1	C	0.888	0.527	-0.172	2 6 11
2	C	-0.203	1.197	0.372	1 3 12
3	C	-1.382	0.507	0.637	2 4 7
4	C	-1.470	-0.853	0.356	3 5 8
5	C	-0.379	-1.522	-0.190	4 6 9
6	C	0.800	-0.832	-0.453	1 5 10
7	H	-2.240	1.034	1.066	3
8	H	-2.397	-1.396	0.565	4
9	H	-0.448	-2.592	-0.411	5
10	H	1.659	-1.359	-0.881	6
11	H	1.815	1.071	-0.380	1
12	H	-0.135	2.267	0.592	2

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\benzene...

File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ?

benzene.pdb

```
1 HETATM 1 C 1 0.888 0.527 -0.172
2 HETATM 2 C 2 -0.203 1.197 0.372
3 HETATM 3 C 3 -1.382 0.507 0.637
4 HETATM 4 C 4 -1.470 -0.853 0.356
5 HETATM 5 C 5 -0.379 -1.522 -0.190
6 HETATM 6 C 6 0.800 -0.832 -0.453
7 HETATM 7 H 7 -2.240 1.034 1.066
8 HETATM 8 H 8 -2.397 -1.396 0.565
9 HETATM 9 H 9 -0.448 -2.592 -0.411
10 HETATM 10 H 10 1.659 -1.359 -0.881
11 HETATM 11 H 11 1.815 1.071 -0.380
12 HETATM 12 H 12 -0.135 2.267 0.592
13 CONECT 1 2 6 11
14 CONECT 2 1 3 12
15 CONECT 3 2 4 7
16 CONECT 4 3 5 8
17 CONECT 5 4 6 9
18 CONECT 6 1 5 10
19 CONECT 7 3
20 CONECT 8 4
21 CONECT 9 5
22 CONECT 10 6
23 CONECT 11 1
24 CONECT 12 2
```

length Ln: 1 Col: 1 Sel: 0 | 0 Windows (CR LF) UTF-8 INS

Creating and Running Jobs

CalcALC: Muon ALC, QLCR and LF decoupling for molecular systems using SCARF (v1.01)

Setup Jobs Results Spectrum

Load Molecule

Click: non-H sites for addition
H-sites for substitution

Name for job set:
benzene

Make Job Set

Site	Atom	x	y	z	Bonds to
1 *	C	0.888	0.527	-0.172	2 6 11
2	C	-0.203	1.197	0.372	1 3 12
3	C	-1.382	0.507	0.637	2 4 7
4	C	-1.470	-0.853	0.356	3 5 8
5	C	-0.379	-1.522	-0.190	4 6 9
6	C	0.800	-0.832	-0.453	1 5 10
7	H	-2.240	1.034	1.066	3
8	H	-2.397	-1.396	0.565	4
9	H	-0.448	-2.592	-0.411	5
10	H	1.659	-1.359	-0.881	6
11	H	1.815	1.071	-0.380	1
12	H	-0.135	2.267	0.592	2

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\benzene.pdb

Setup DFT

DFT Method B3LYP

Basis set 6-31G(d,p)

Pre-optimize structure with PM3
 Pre-optimize structure with PM6
 Optimize structure with DFT
 Calculate EFG
 Reference state without the muon

Spin state doublet

Charge state 0

SCARF username fp63

Processor cores 4

Max run time (hours) 4

Gaussian DFT Jobs

JOB-ID	STATUS	EXEC-HOST	JOB-NAME	SUBMIT-TIME	RUN-TIME
672981	RUN	4*cn442.scarf.rl.ac.uk	benzene-add1_PM3opt_B3LYP_6-31G_d_p_doublet_charge_0	22:10	0:00:40

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

Results Table Window

Gaussian DFT Jobs

JOB-ID	STATUS	EXEC-HOST	JOB-NAME	SUBMIT-TIME	RUN-TIME
672981	DONE	4*cn442.scarf.rl.ac.uk	benzene-add1_PM3opt_B3LYP_6-31G_d_p_doublet_charge_0	22:10	0:01:22

Submit Jobs to SCARF

Clear non-running jobs

Remove Completed Jobs from List

Kill All Submitted Jobs

Job polling:

Hyperfine Parameters from the DFT Output

Load DFT output

Energy (eV): -6334.887

Set E0

Click on atoms to select nuclei to include in spectrum

Show deuteration

Include minor isotopes

Muon site: 13

Muon Site Quantum/Calibration Factors

A 1.230 D1 1.000 D2 1.000 Auto

Nuclear Site Quantum/Calibration Factors

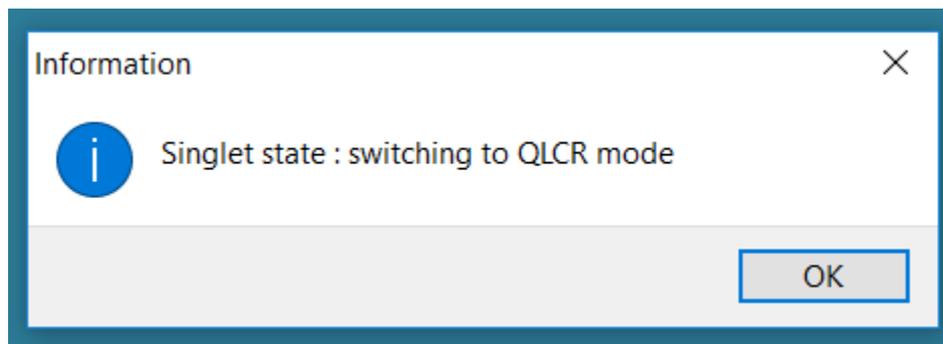
A 1.000 D1 1.000 D2 1.000

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
13	Mu	0.06392	595.9	15.0	11.1	21876			212.6		
11	H	0.06405	152.4	4.7	3.5		23719	147.0	54.4		
9	H	0.00797	11.1	5.2	2.6		31346	17.5	4.0		
7	H	0.00797	11.1	5.2	2.6		31346	17.5	4.0		
12	H	-0.02136	-30.6	17.5	14.8		33596	25.9	10.9		
10	H	-0.02136	-30.6	17.5	14.8		33596	25.9	10.9		
8	H	-0.02672	-37.8	20.8	20.1		33984	29.7	13.5		

Add radical to ALC spectrum table

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\benzene-add1_PM3opt_B3LYP_6-31G_d_p_doublet_charge_0.out

Results Table Window: QLCR Mode



 Dipolar/Quadrupolar Parameters from the DFT Output (singlet state) ? X

Load DFT output

Energy (eV): -2985.894 Set E0

Click on atoms to select nuclei to include in spectrum Muon site: 3

Show deuteration Include minor isotopes

Site number	Atom	Isotope	I	x	y	z	ω -Dip (MHz)	B-Dip (G)	B-QLCR (G)	NQCC (MHz)	η
3	Mu		0.5	0	0	0					
1	N		1.0	0.00	0.00	-0.99	0.263	3.1	26.2	0.473	0.000
2	N		1.0	0.00	0.00	-2.09	0.028	0.3	278.3	5.028	0.000

Add muon state to QLCR spectrum

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\N2\N2-Muplus-add1_PM3opt_B3LYP_cc-pVDZ_singlet_charge_1_EFG.out

Spectrum Table Window

Hyperfine Parameters from the DFT Output

Load DFT output

Energy (eV): -18480.983 Set E0

Click on atoms to select nuclei to include in spectrum Muon site: 21

Show deuteration Include minor isotopes

Muon Site Quantum/Calibration Factors
 A D1 D2 Auto

Nuclear Site Quantum/Calibration Factors
 A D1 D2

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
13	N	1.27442	59.1	64.9	48.5		20282	67.1	21.1		
21	Mu	0.07756	599.5	53.9	19.4	22010			213.9		
14	N	0.15706	7.1	11.5	1.9		22255	13.1	2.5		
15	N	-0.16641	-7.5	-12.6	1.9		22807	13.2	2.7		
16	N	-0.16700	-7.5	-12.7	1.9		22809	13.2	2.7		
17	H	0.00694	11.7	6.5	4.4		31508	17.7	4.2		
20	H	0.00659	10.4	-4.3	3.8		31581	17.2	3.7		
19	H	-0.00540	-8.6	4.4	2.3		32605	16.6	3.1		
18	H	-0.02239	-15.9	42.9	7.2		33002	19.0	5.7		

Add radical to ALC spectrum table

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\tcnq\tcnq-add9_PM3opt_B3LYP_cc-pVDZ_doublet_charge_0.out

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
2		Mu	21	487.40	1.230	599.5	53.90	1.000	53.9	19.40	1.000	19.4	1.000

Global Factors

A-Mu D1-Mu D2-Mu Resonance set of single radical

A-nuc D1-nuc D2-nuc

Clear Table

Calculating and Plotting ALC/QLCR Spectra

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
2		Mu	21	487.40	1.230	599.5	53.90	1.000	53.9	19.40	1.000	19.4	1.000

Global Factors

A-Mu D1-Mu D2-Mu
A-nuc D1-nuc D2-nuc

Resonance set of single radical

ALC Spectrum Generation

Field Range and Steps

Bmin
Bmax
Bstep

Broadening

2 %
 50 G
 no broadening

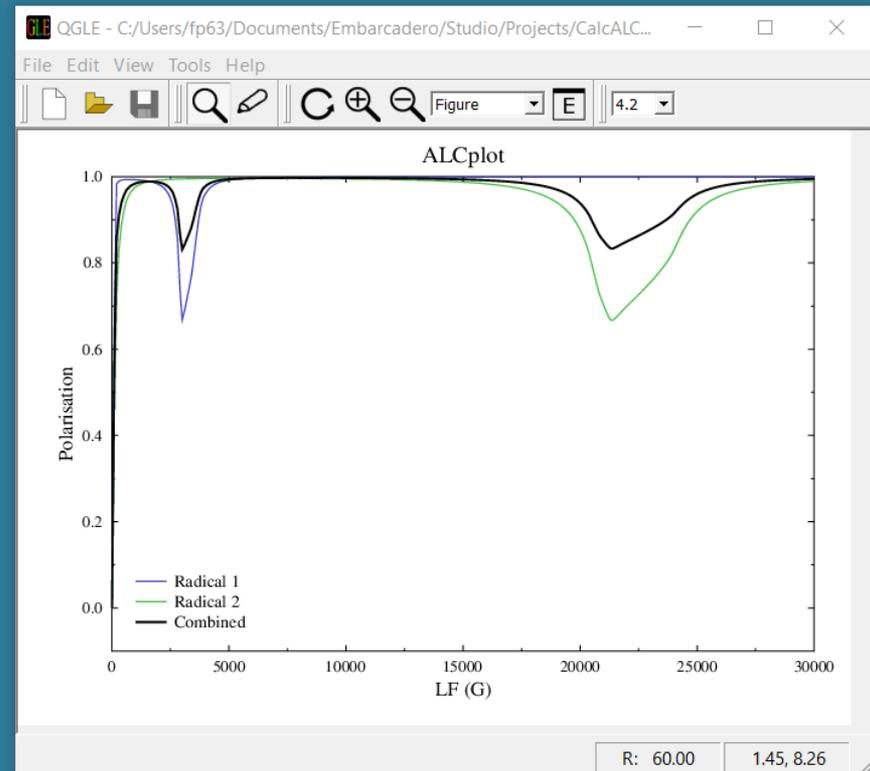
Time Range (microseconds)

From To

Plot name:

Orientational averaging steps

Solid State
 Liquid State



Fine Tuning Spectral Plots: Python and GLE files

GLE	ALCplot.gle	GLE Script	1 KB
	ALCplot-rad2.tab	TAB File	4 KB
	ALCplot-rad1.tab	TAB File	4 KB
	ALCplot-rad2.py	PY File	2 KB
	ALCplot-rad1.py	PY File	2 KB

```
ALCplot-rad1.py x
1 from quantumtools2 import *
2 from math import *
3 fAMu=1.00000
4 fD1Mu=1.00000
5 fD2Mu=1.00000
6 fAn=1.00000
7 fD1n=1.00000
8 fD2n=1.00000
9 bin0=0.00
10 bin1=8.00
11 Bmin=0.00
12 Bmax=30000.00
13 Bstep=200.00
14 npcr=100
15 Gmu=0.01355
16 Ge=-2.802495266
17 Amu=69.84*1.23000*fAMu
18 D1mu=10.80*1.00000*fD1Mu
19 D2mu=2.70*1.00000*fD2Mu
20 spmat=createSpinMat([2,2])
21 f=open('ALCplot-rad1.tab','w')
22 print 'ALCplot-rad1.tab'
23 npts=int(round((Bmax-Bmin)/Bstep))
24 for i in range(npts+1):
25     print "\r point",i,"of",npts," ",
26     Bmag=Bmin+Bstep*i
27     sum=0
28     for (field,beam,detector,rf) in uniformLF(npchr):
29         rho0=createInitialDensMat(spmat[0],beam)
30         scint=createDetectorOp(spmat[0],detector)
31         Ham=numpy.zeros_like(spmat[0,0,:,:])
32         addZeeman(Ham,spmat[0],field,Gmu*Bmag)
33         addZeeman(Ham,spmat[1],field,Ge*Bmag)
34         addHyperfine(Ham,spmat[0],spmat[1],NonAxialHFT(Amu,D1mu,
35             D2mu,[0.779,-0.625,-0.044],[0.341,0.364,0.867]))
36         (omega,ccos,csin)=solveDensityMat(Ham,rho0,scint)
37         y=evaluateIntoBinsNewLoops(omega,ccos,csin,0.454,[bin0,bin1
38             ])
39         sum=sum+y[0]
40     f.write("{:7.5f} {:8.6f}\n".format(Bmag,sum/npchr))
41     f.close()
42 f=open('gcomplete','w')
43 f.close()
```

```
ALCplot.gle x
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 w1=1.00
9 w2=1.00
10 xmn=0.00
11 xmx=30000.00
12 amove -2 -1
13 begin graph
14 size 35 24
15 title "ALCplot"
16 xtitle "LF (G)"
17 ytitle "Polarisation"
18 xaxis min xmn max xmx hei hh
19 xticks length tt
20 yaxis hei hh
21 xticks length tt
22 data "ALCplot-rad1.tab"
23 d1 smooth lstyle 1 lwidth lw color rgb255(64,64,191) key "Radical 1"
24 data "ALCplot-rad2.tab"
25 d2 smooth lstyle 1 lwidth lw color rgb255(64,191,64) key "Radical 2"
26 let d99 = 1+(w1*(d1-1)+w2*(d2-1))/(w1+w2)
27 d99 smooth lstyle 1 lwidth lw+0.03 color black key "Combined"
28 key nobox pos b1 hei hh-0.1 offset 0.5 0.5
29 end graph
30
```

Future Additions

a) Input formats

- Molecule structure from other file formats
- Reading output from other DFT codes, e.g. Quantum Espresso

b) Site handling

- Averaging hyperfine/quadrupolar parameters for groups of sites
- Treatment of site pairs

c) QLCR mode

- Better handling of isotopes
- Treatment of quantum corrections for the EFG

d) Longer term

- Include measured data in plots and allow parameter fitting
- Extend towards periodic systems



Summary

CalcALC provides an easy way to rapidly estimate ALC and QLCR spectra

Hybrid SE/DFT method produces results in minutes to hours
(Pure DFT/DFT method needs hours to days)

CalcALC is available at the website:

<http://shadow.nd.rl.ac.uk/calcalc>

Please contact me at francis.pratt@stfc.ac.uk if in need of any help
and also to provide your valuable feedback