Science & Technology Facilities Council
ISIS

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

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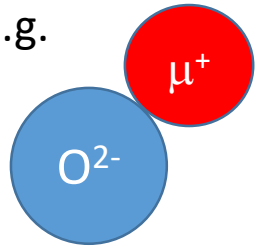
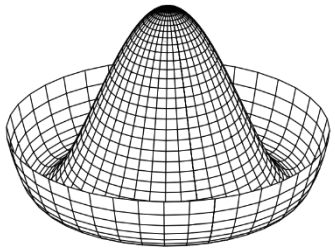
Energy Landscape and Quantum Effects

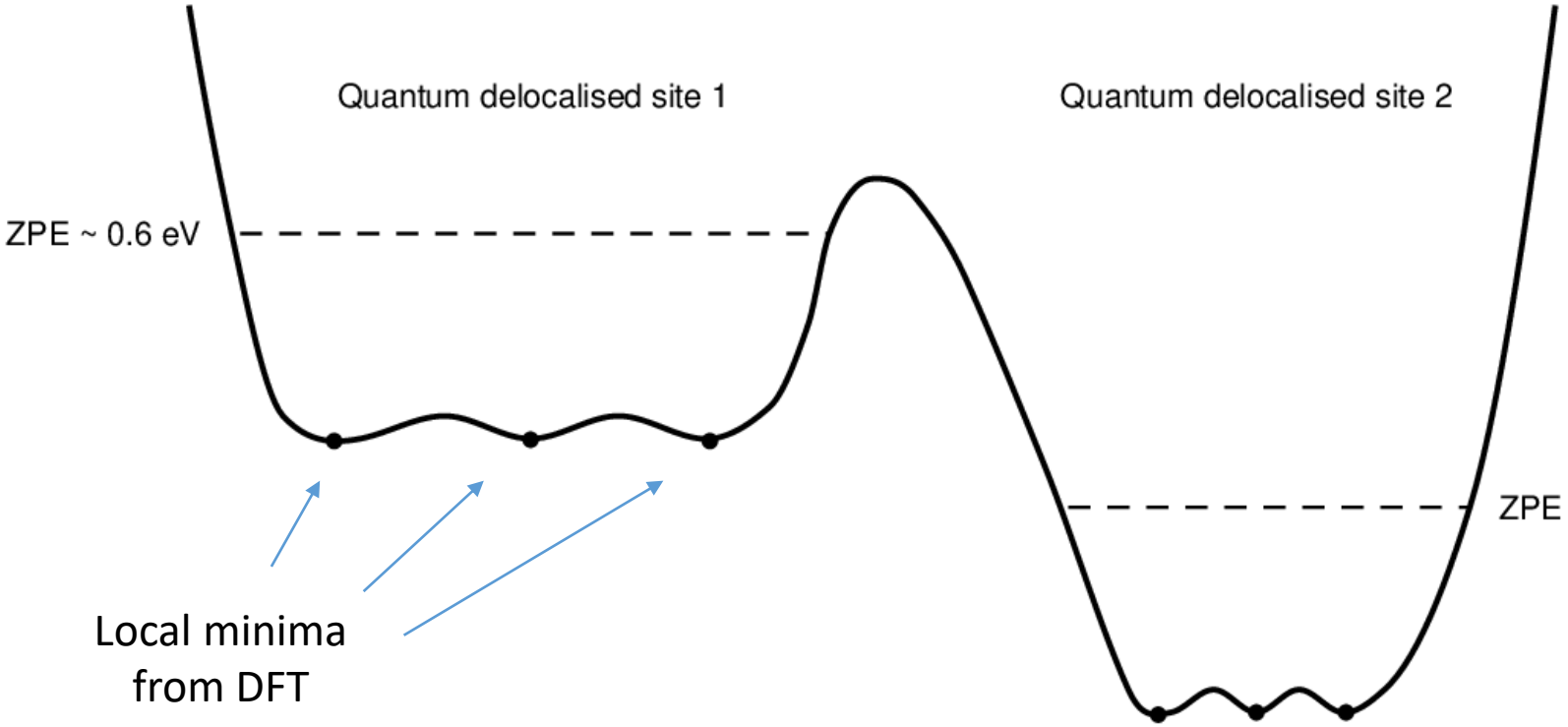
e.g.





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

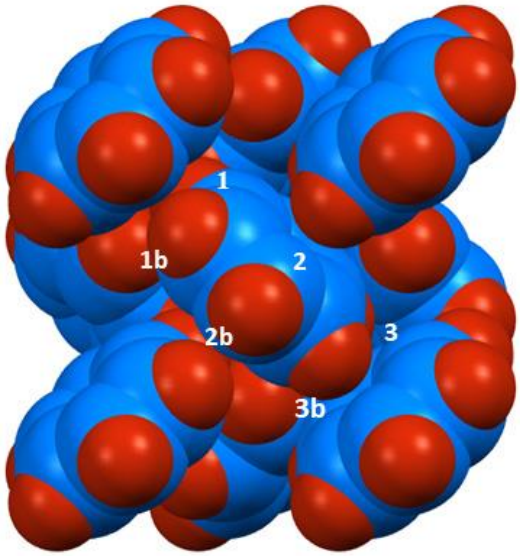
Rotation modes may also shift A significantly, e.g. the QF is found to be -150% for muoniated acetone $(CH_3)_2CO$-Mu

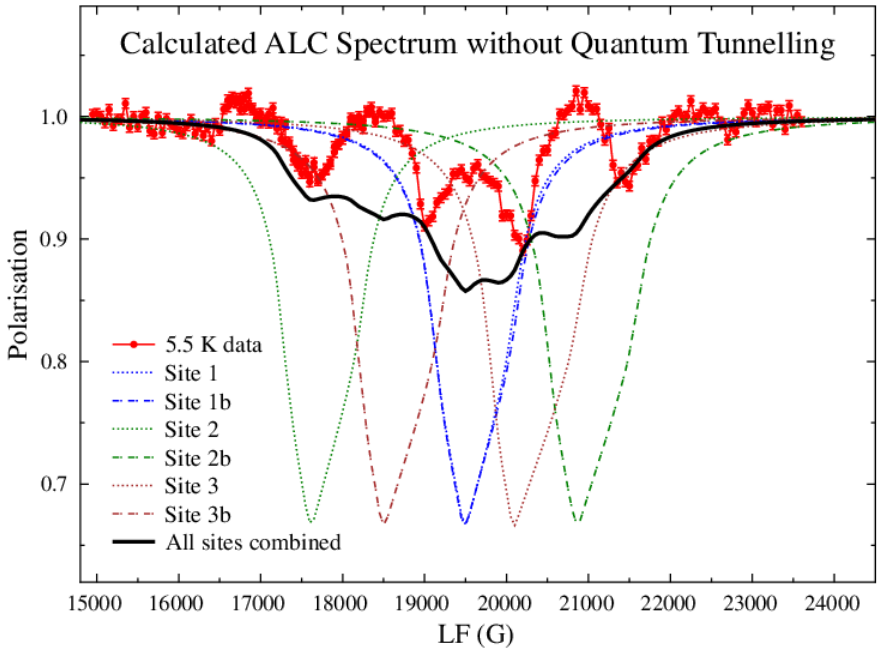


Example of ALC in Solid Benzene

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

CalcALC simulates the corresponding ALC spectra



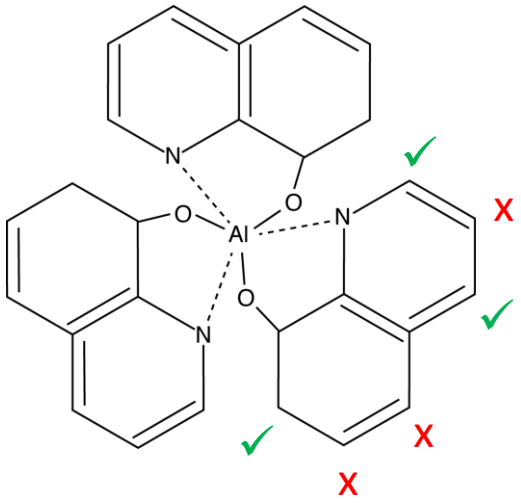


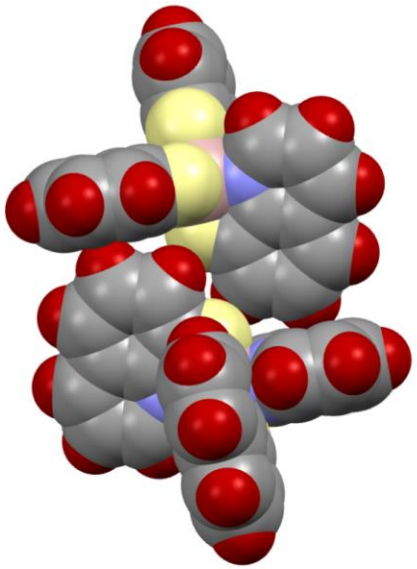
Quantum tunnelling of radical states is needed to describe the ALC spectra at low temperatures

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

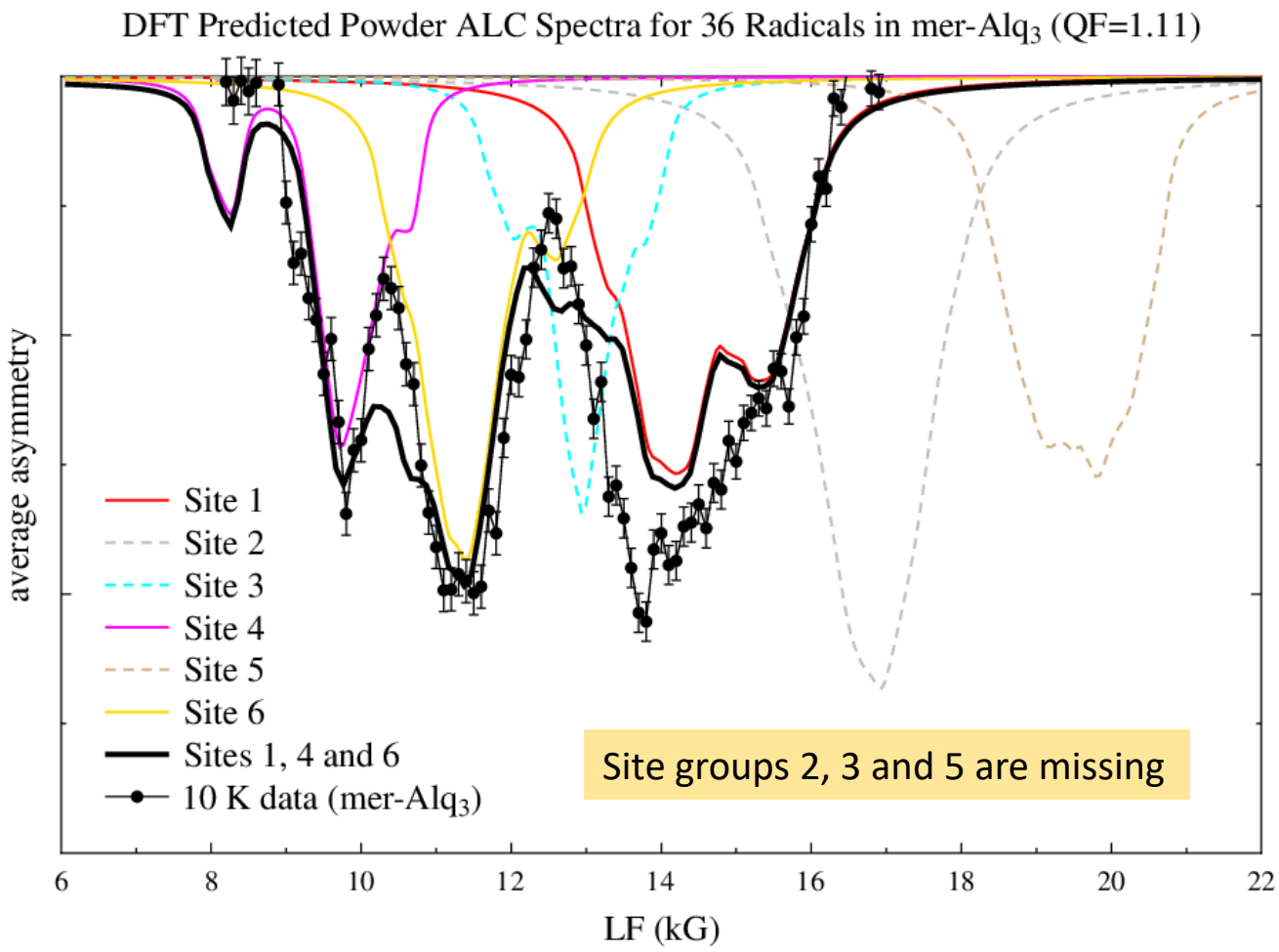
An entangled state of the muon, the electron and two protons is involved in the tunnelling

A more Complicated Molecule: Alq3



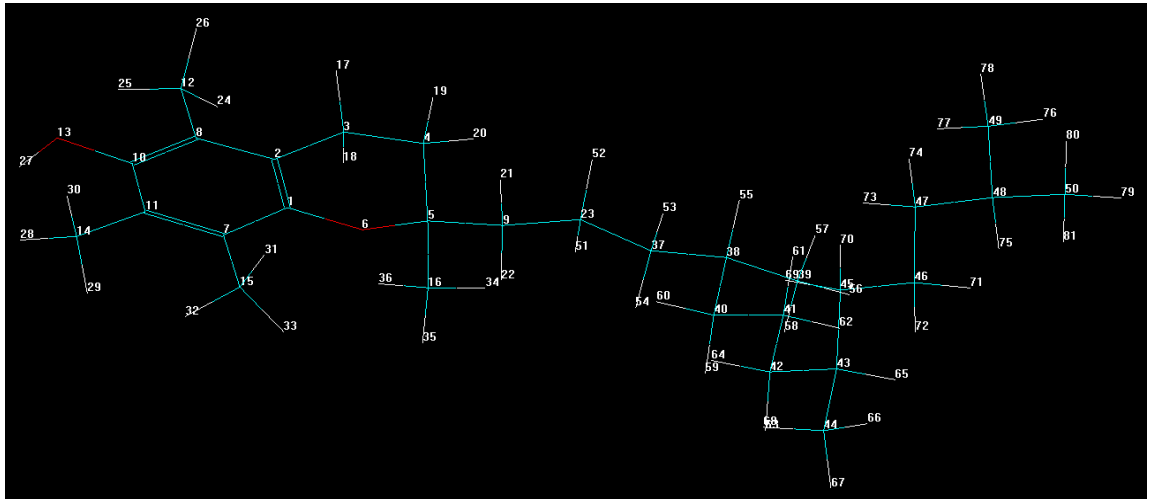


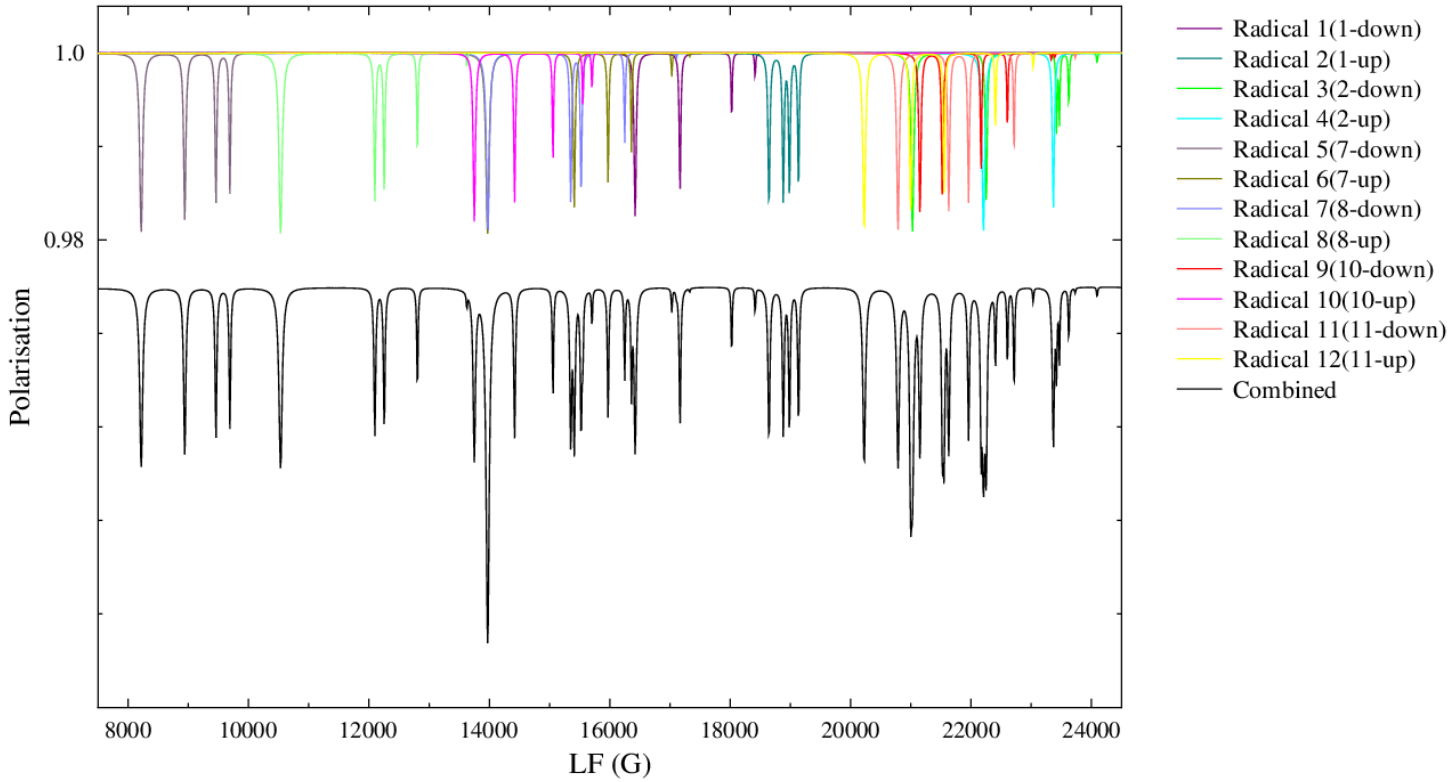
At least 36 distinct sites are possible



Site groups 2, 3 and 5 are missing

Even more complex: Δ_0 ALC Spectrum for Vitamin E





Diamagnetic Muon States: QLCR

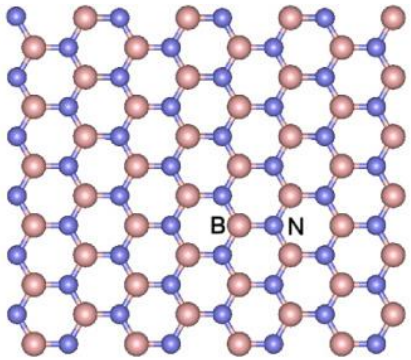
QLCR is a cross-relaxation between:

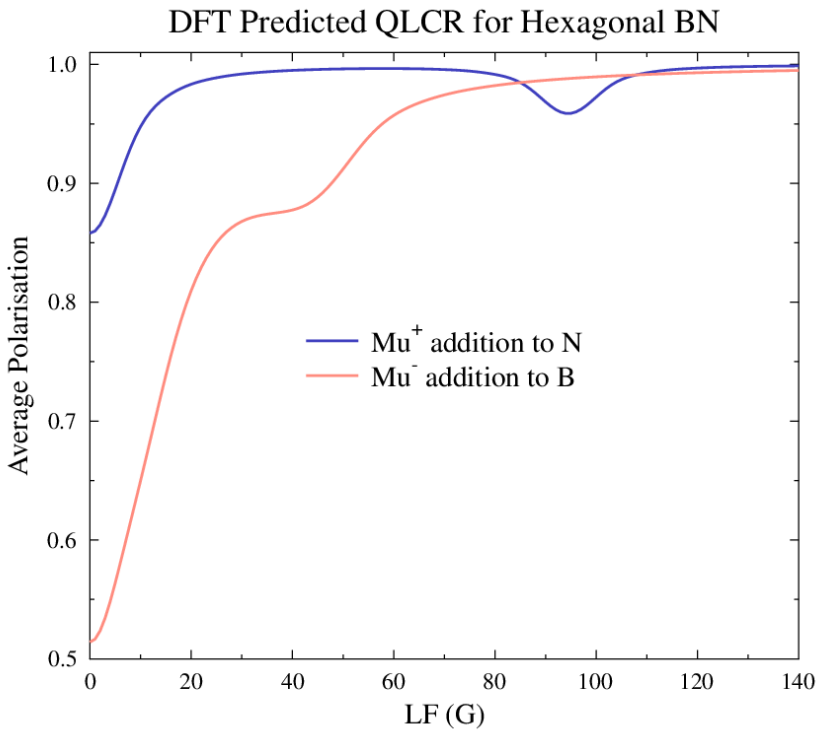
Muon Zeeman Splitting	and	Nuclear quadrupole splitting

Quadrupole splittings depend on:

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

Hexagonal BN





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:

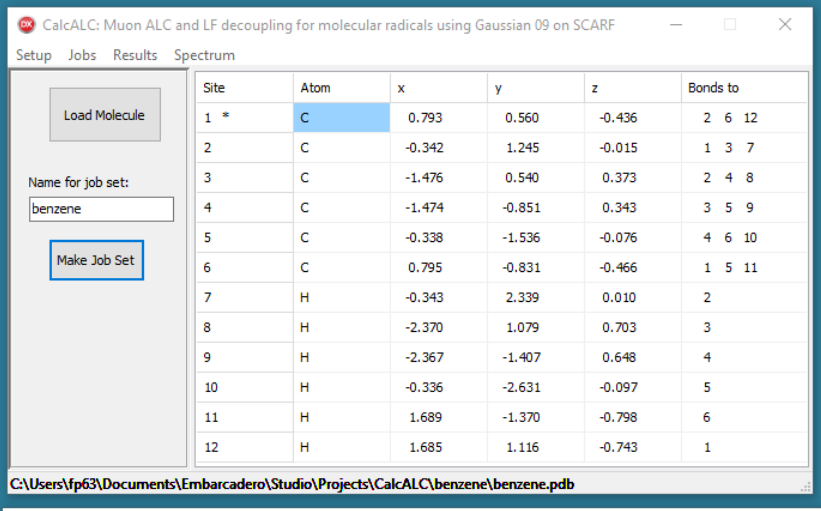
1) Input molecular structure from a file in pdb format
2) Selection of muon addition or substitution sites, DFT method, charge, spin states etc.
3) Preparation of a set of Gaussion09 jobs for different sites
4) Job submission to SCARF, monitoring of progress and return of output files
5) Hyperfine and 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

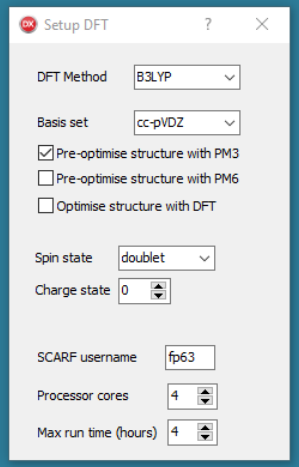
Requirements:

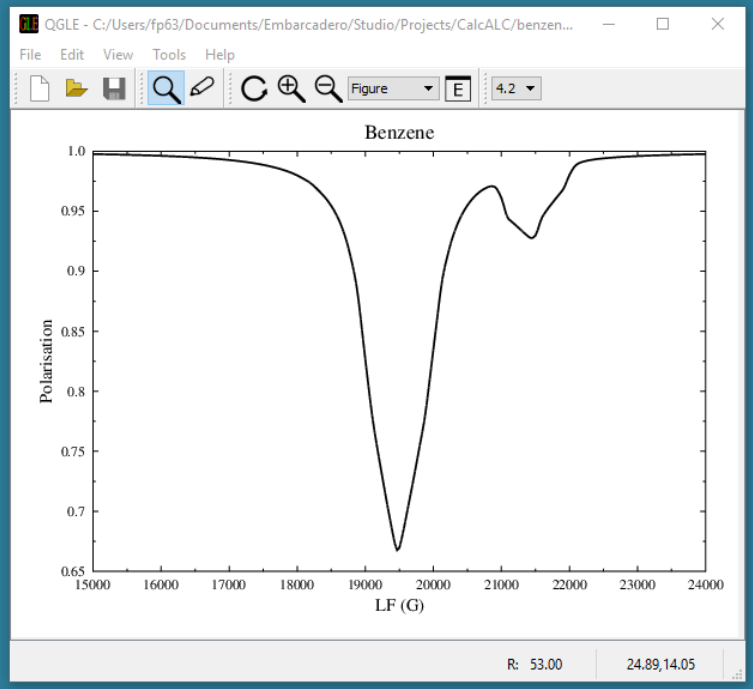
1) A Windows PC or a Windows virtual machine
2) A user account on the STFC compute cluster SCARF
3) Scp and ssh functions provided by the Putty package
4) Python 2.7 as provided by a Mantid installation for running Quantum
5) GLE as included in a WiMDA installation for plotting the spectra

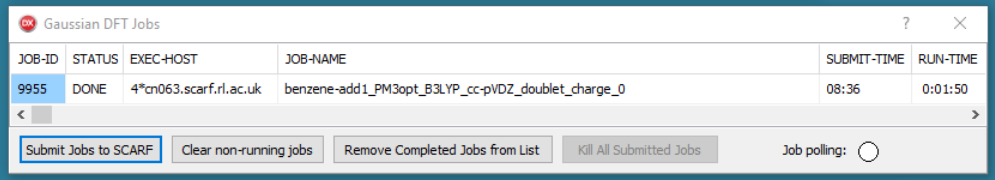
Website: http://shadow.nd.rl.ac.uk/calcalc

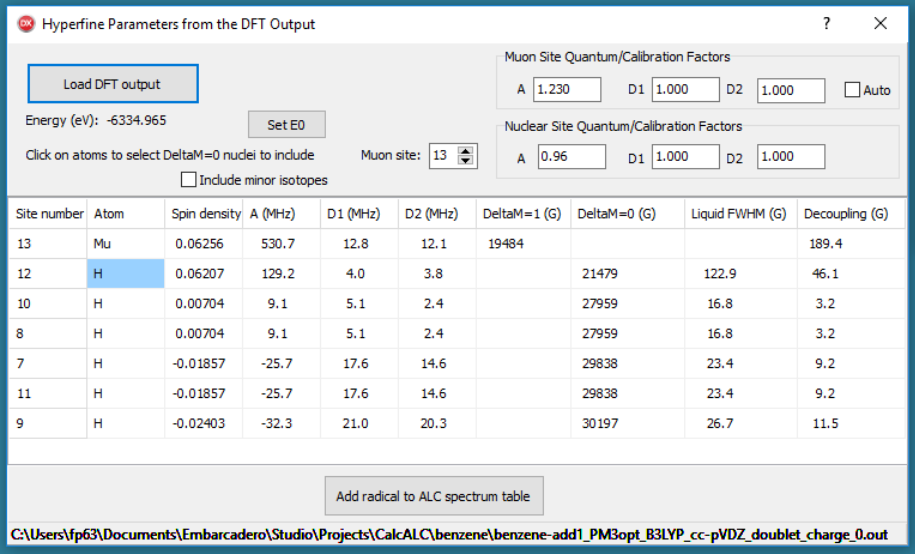
CalcALC: From Molecule to ALC Spectrum via DFT

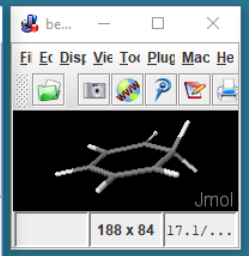


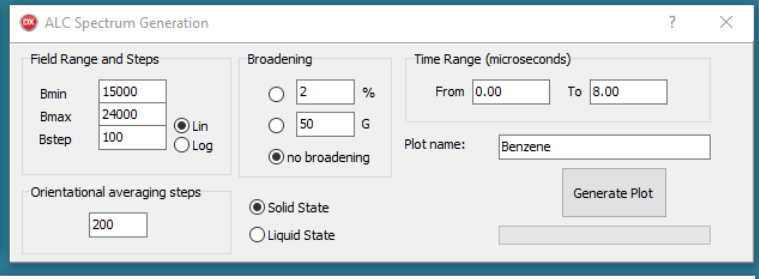


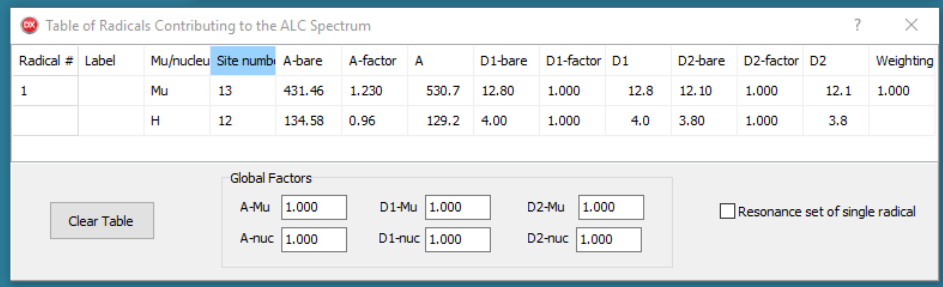








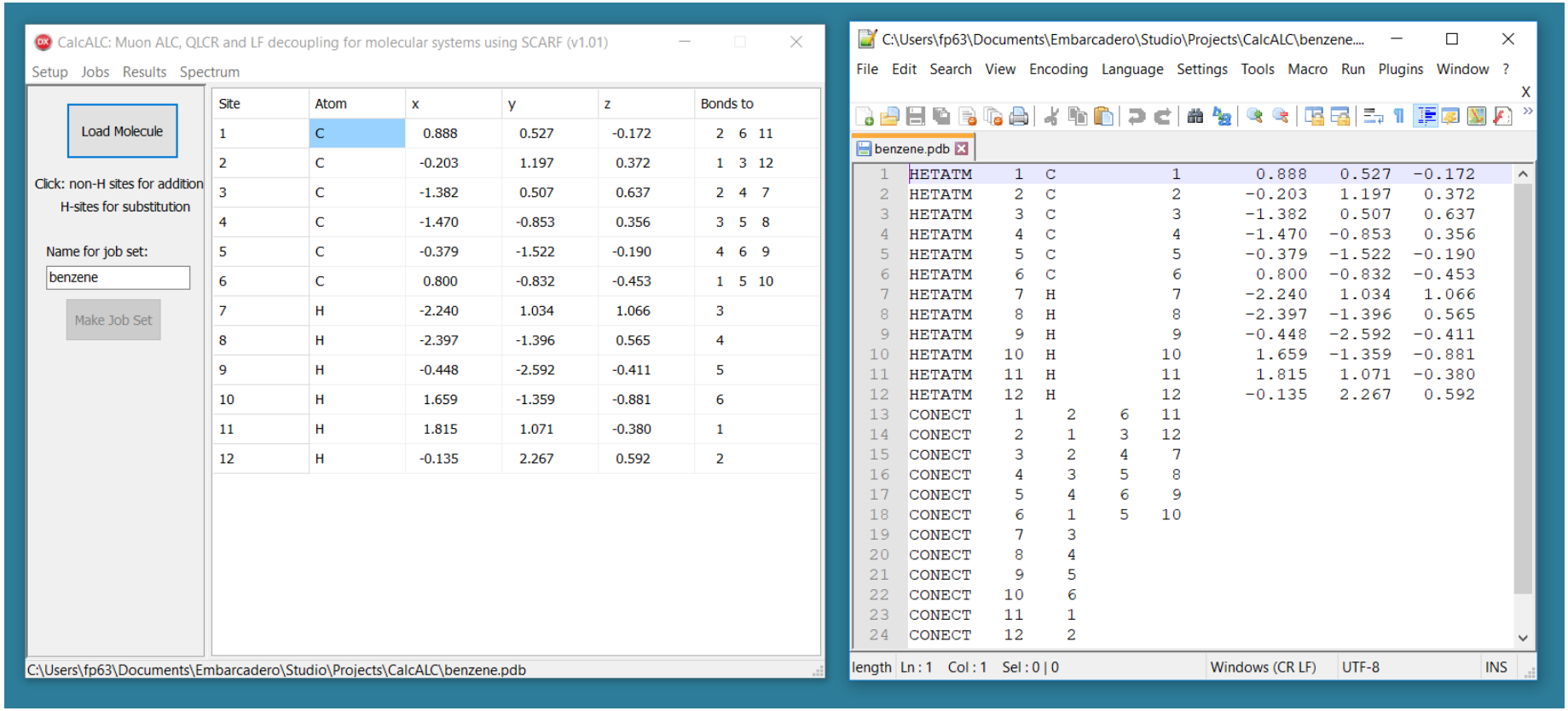




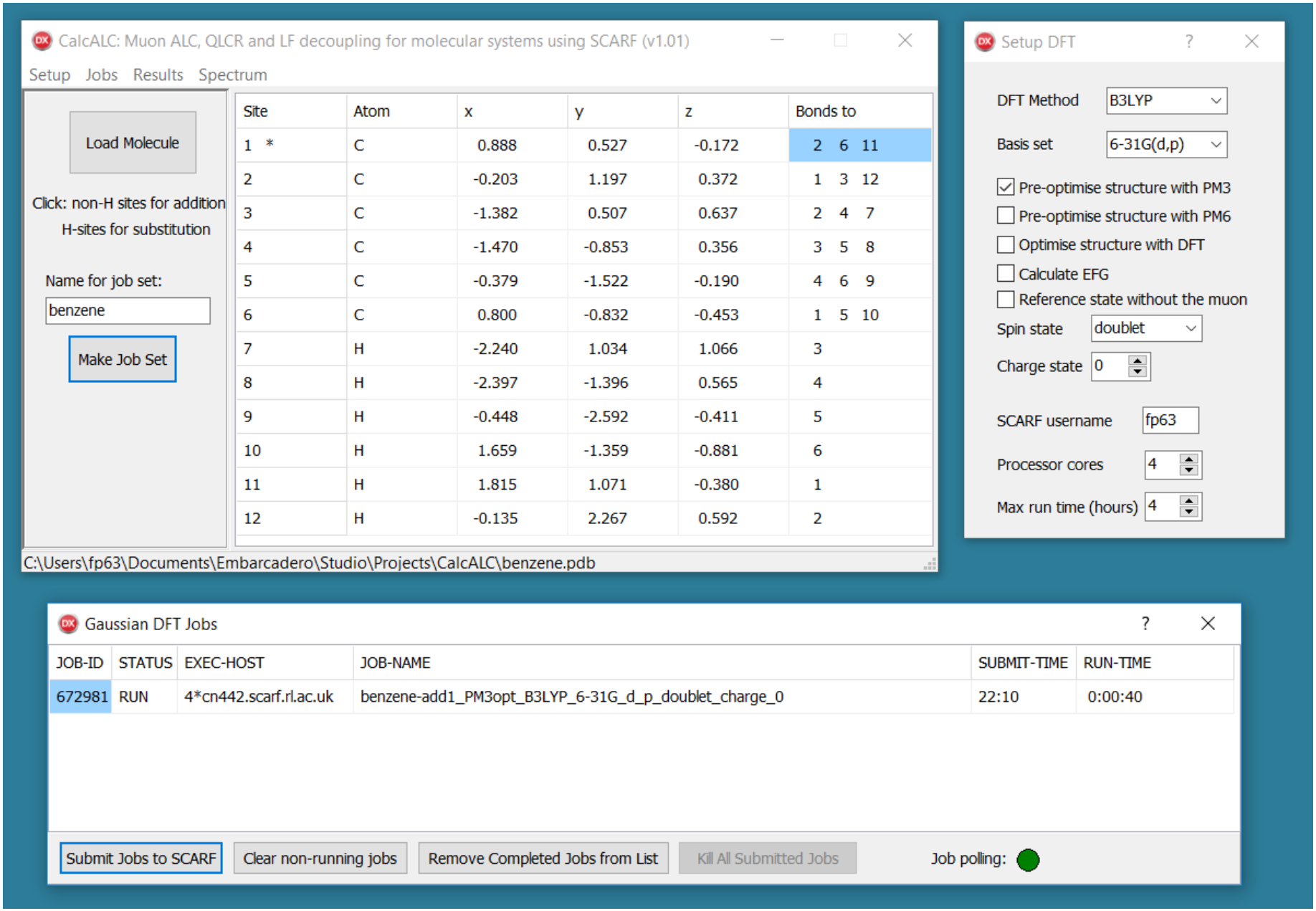
Input Structure Files

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

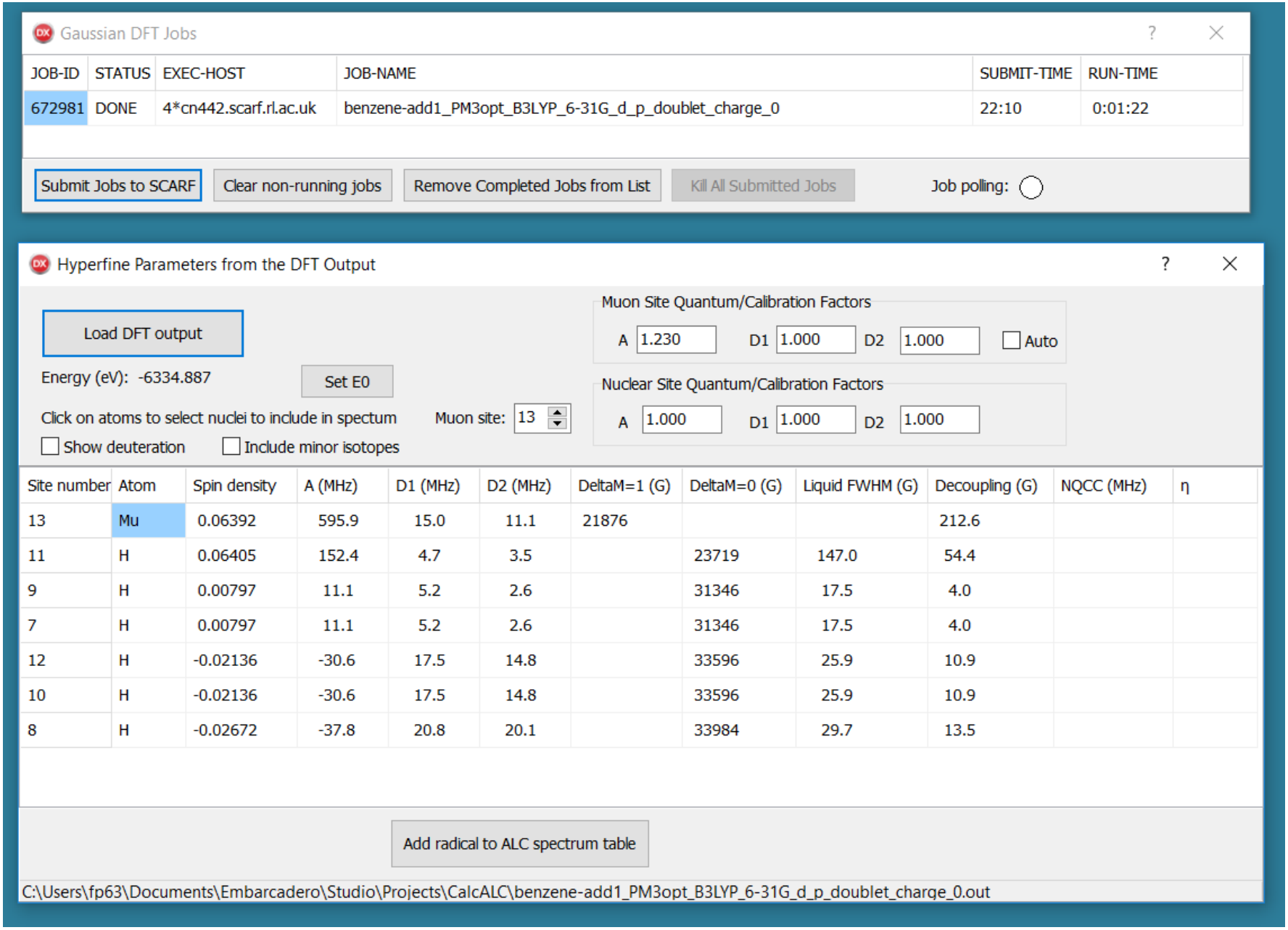
The OpenBabel utility is available to convert from other structure formats



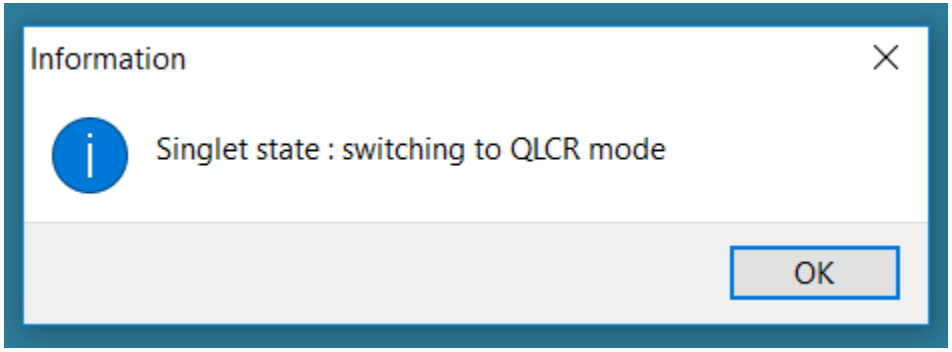
Creating and Running Jobs



Results Table Window



Results Table Window: QLCR Mode



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

Load DFT output

Energy (eV): -2985.894

Set E0

Click on atoms to select nuclei to include in spectum

Muon site: 3

Show deuteration

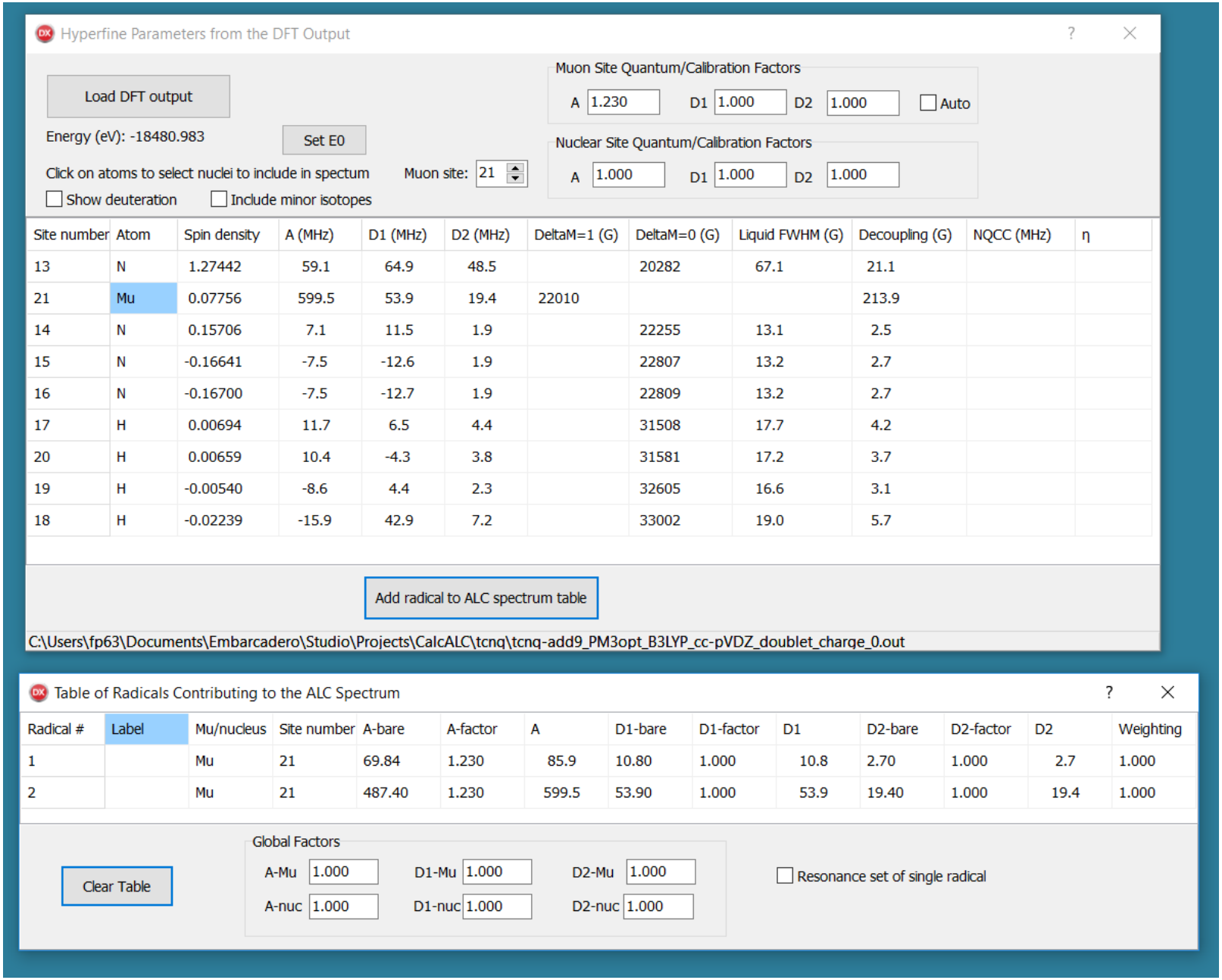
Include minor isotopes

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



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

Clear Table

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 single radical

ALC Spectrum Generation

Field Range and Steps

Bmin 0

Bmax 30000

Bstep 200

Lin / Log

Broadening

2 %

50 G

no broadening

Time Range (microseconds)

From 0.00 To 8.00

Plot name: ALCplot

Generate Plot

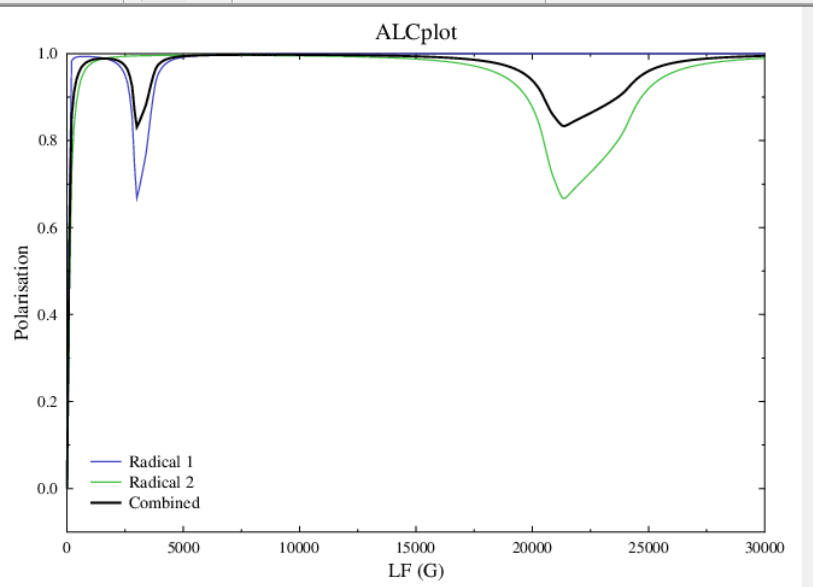
Orientational averaging steps

100

Solid State / Liquid State

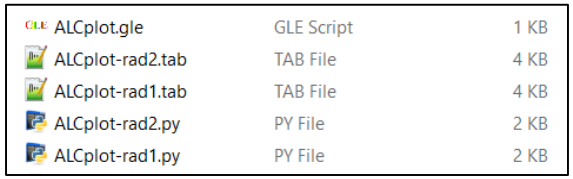
QGLE - C:/Users/fp63/Documents/Embarcadero/Studio/Projects/CalcALC...

File Edit View Tools Help



R: 60.00 1.45, 8.26

Fine Tuning Spectral Plots: Python and GLE files



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

```
from quantumtools2 import *
from math import *
fAMu=1.00000
fD1Mu=1.00000
fD2Mu=1.00000
fAn=1.00000
fD1n=1.00000
fD2n=1.00000
bin0=0.00
bin1=8.00
Bmin=0.00
Bmax=30000.00
Bstep=200.00
npcr=100
Gmu=0.01355
Ge=-2.802495266
Amu=69.84*1.23000*fAMu
D1mu=10.80*1.00000*fD1Mu
D2mu=2.70*1.00000*fD2Mu
spmat=createSpinMat([2,2])
f=open('ALCplot-rad1.tab',"w")
print 'ALCplot-rad1.tab'
npts=int(round((Bmax-Bmin)/Bstep))
for i in range(npts+1):
 print "\r point",i,"of",npts,"    ",
 Bmag=Bmin+Bstep*i
 sum=0
 for (field,beam,detector,rf) in uniformLF(npcr):
  rho0=createInitialDensMat(spmat[0],beam)
  scint=createDetectorOp(spmat[0],detector)
  Ham=numpy.zeros_like(spmat[0,0,:,:])
  addZeeman(Ham,spmat[0],field,Gmu*Bmag)
  addZeeman(Ham,spmat[1],field,Ge*Bmag)
  addHyperfine(Ham,spmat[0],spmat[1],NonAxialHFT(Amu,D1mu,
  D2mu,[0.779,-0.625,-0.044],[0.341,0.364,0.867]))
  (omega,ccos,csin)=solveDensityMat(Ham,rho0,scint)
  y=evaluateIntoBinsNewLoops(omega,ccos,csin,0.454,[bin0,bin1
  ])
  sum=sum+y[0]
 f.write("{:7.5f} {:8.6f}\n".format(Bmag,sum/npcr))
f.close()
f=open('qcomplete',"w")
f.close()
```

ALCplot.gle

```
size 29 21
set font rm
hh=0.7
ht=0.7
set hei ht
set lwidth 0.03
lw=0.04
w1=1.00
w2=1.00
xmn=0.00
xmx=30000.00
amove -2 -1
begin graph
size 35 24
title "ALCplot"
xtitle "LF (G)"
ytitle "Polarisation"
xaxis min xmn max xmx hei hh
xticks length tt
yaxis hei hh
xticks length tt
data "ALCplot-rad1.tab"
d1 smooth lstyle 1 lwidth lw color rgb255(64,64,191) key "Radical 1"
data "ALCplot-rad2.tab"
d2 smooth lstyle 1 lwidth lw color rgb255(64,191,64) key "Radical 2"
let d99 = 1+(w1*(d1-1)+w2*(d2-1))/(w1+w2)
d99 smooth lstyle 1 lwidth lw+0.03 color black key "Combined"
key nobox pos bl hei hh-0.1 offset 0.5 0.5
end graph
```

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