Using DFT to Determine Muon Probe States

(with an emphasis on molecular systems)

Francis Pratt

ISIS Muon Group

Outline of Lecture

1) Finding muon sites (single molecule or crystal)
2) Muon coupling at these sites (dipolar and contact hyperfine interactions)
3) Quantum (zero-point) and thermal motion of the muon
4) Molecular dynamics via ALC
5) Electron dynamics via LF relaxation
6) Electronic order
7) Large systems
8) Disordered systems

Workshop N: hands-on session with CalcALC, MuFinder and DipoleCalc

Finding Muon Sites

Muon AIRSS approach:	generate a set of random starting position relax the structures for the set organise the results into groups of sites evaluate magnetic properties (hyperfine parameters)
Molecular systems:	use knowledge of chemical bonding for Mu addition relax structures using fast semi-empirical methods, e.g. PM3 or DFTB+ (these are based on training set data)

Note that the training sets for the semi-empirical methods rely on molecular structures and energetics, not the distribution of spin density

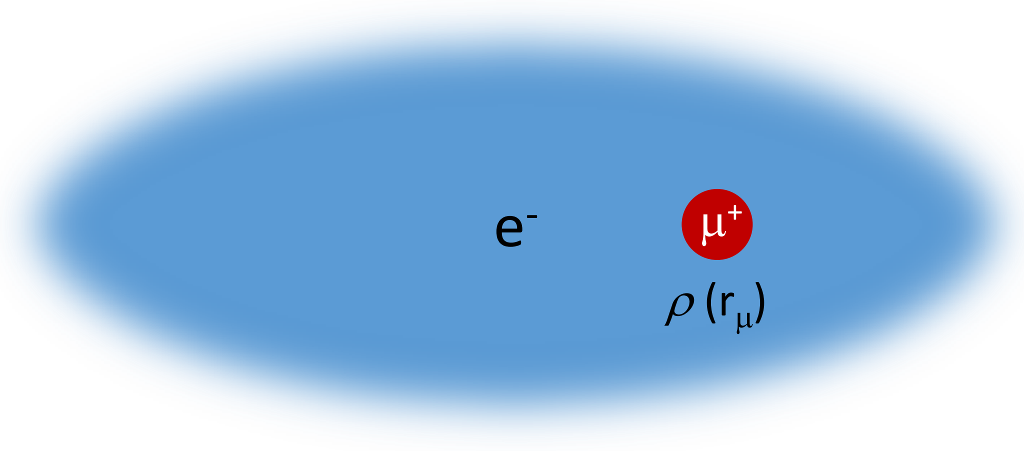
DFT should be used for determining reliable electronic structure properties at the relaxed geometries provided by the semi-empirical methods

Coupling of the Muon to Electronic Spins

Isotropic Fermi contact hyperfine coupling:

$$A = \frac{2\mu_0}{3}\gamma_\mu \gamma_e \rho(\mathbf{r}_\mu)$$

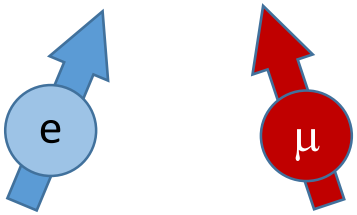
$$\rho(r_\mu) = \rho_\uparrow(r_\mu) - \rho_\downarrow(r_\mu)$$

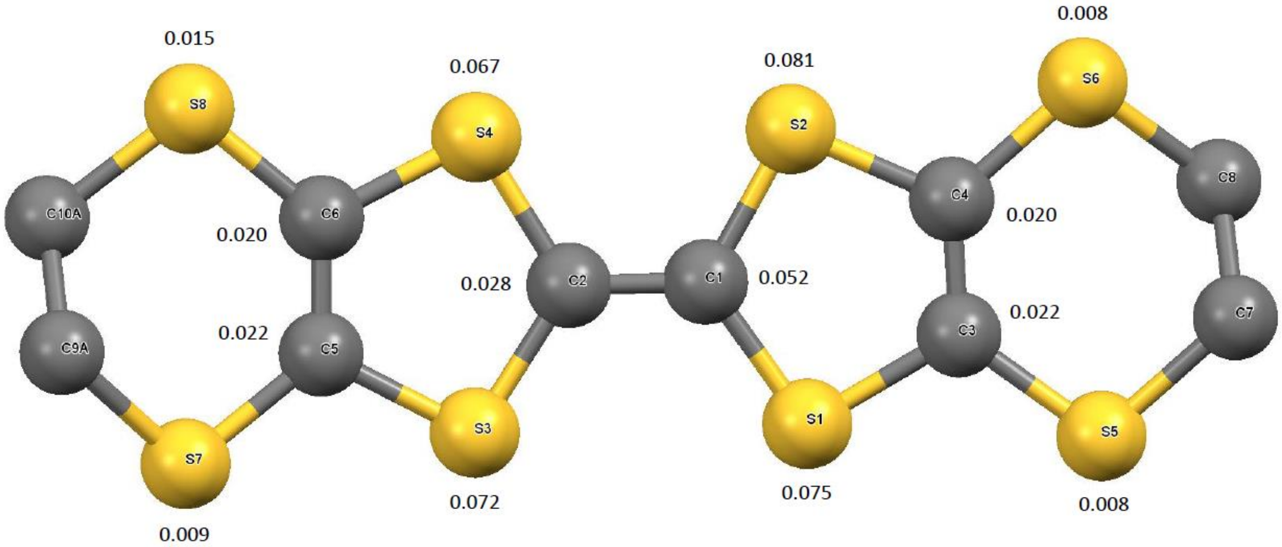


Coupling of the Muon to Electronic Spins

Magnetic dipolar coupling:

$$\mathbf{B}_{\mathrm{dip}}(\mathbf{r}_\mu) = \frac{\mu_0}{4\pi}\sum_i \frac{3(\mathbf{m}_i \cdot \hat{\mathbf{r}}_{i\mu})\hat{\mathbf{r}}_{i\mu} - \mathbf{m}_i}{|\mathbf{r}_\mu - \mathbf{r}_i|^3}$$





Coupling of the Muon to Electronic Spins

Full hyperfine tensor description gives both the

Fermi contact term and the dipolar interaction:

$$\text{Hyperfine tensor} = \underbrace{\begin{pmatrix} A & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & A \end{pmatrix}}_{\text{isotropic}} + \underbrace{\begin{pmatrix} D_1 & 0 & 0 \\ 0 & -D_1/2 & 0 \\ 0 & 0 & -D_1/2 \end{pmatrix}}_{\text{axial dipolar}} + \underbrace{\begin{pmatrix} 0 & 0 & 0 \\ 0 & D_2/2 & 0 \\ 0 & 0 & -D_2/2 \end{pmatrix}}_{\text{non-axial dipolar}}$$

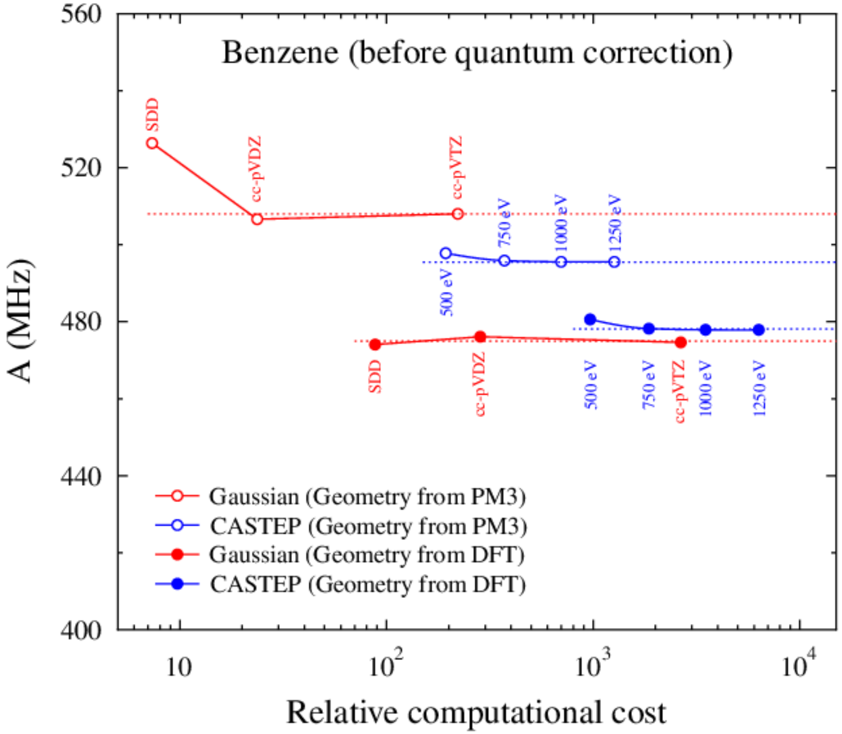
D_1 and D_2 represent a delocalised distribution of spin density
e.g. as found in a molecular radical

Setting $A = 0$ and $D_2 = 0$ reverts to the familiar axial dipolar interaction with a point spin

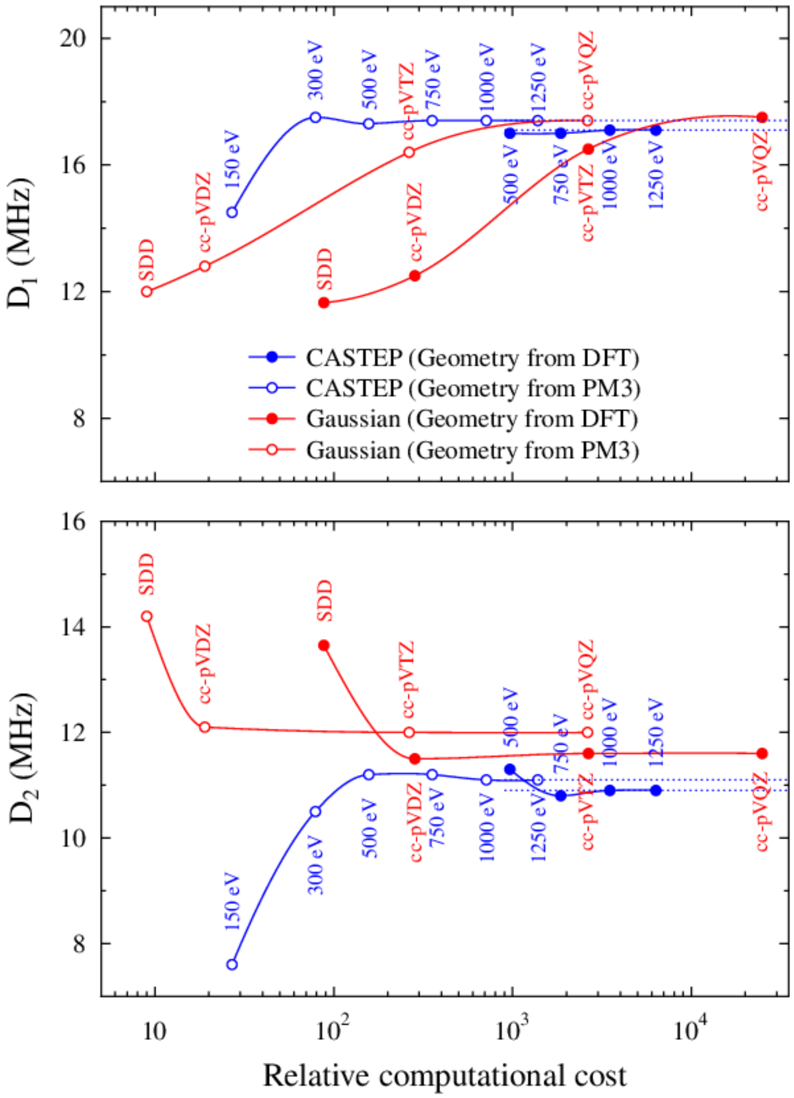
Finding Muon Sites

What size of basis set do I need?

How long will the calculations take?



seconds *minutes* *hours*



Here we have *N* = 13 for benzene+Mu

Computation times are expected to scale as N^3 or $N^2 lnN$

Finding Muon Sites

Some currently recommended methods:

	Single Molecule	**Periodic Crystal**
Semi-empirical method	Hartree-Fock: PM3-PM7 (available in Gaussian)	DFTB+
DFT Code:	Gaussian	CASTEP, Quantum Espresso etc.
Basis set:	cc-pVDZ or larger	Plane waves + ultrasoft pseudopotentials
Functional:	Hybrid functional B3LYP	Generalised Gradient Approximation (PBE)

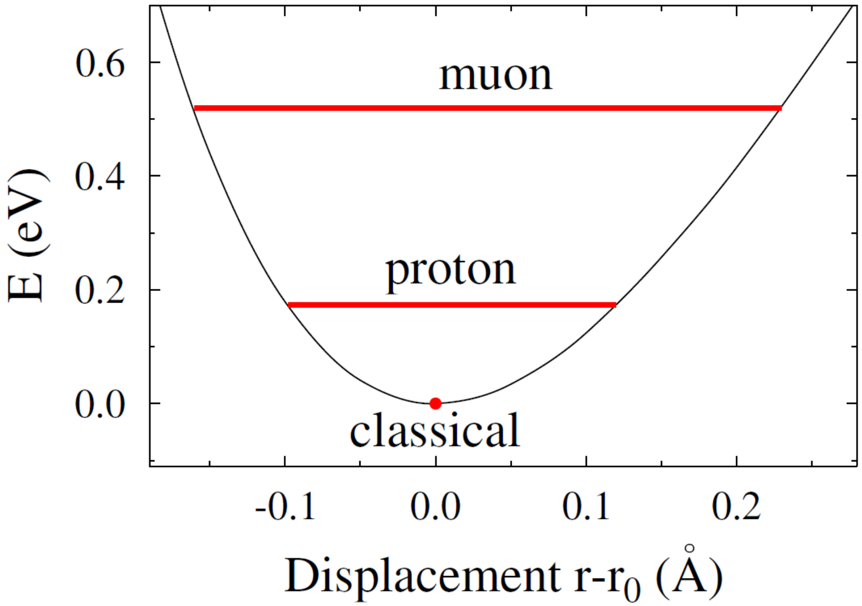
Hybrid approach

Use a semi-empirical method for relaxing the structure followed by a single point DFT calculation for accurate determination of the spin distribution and hyperfine tensor

Much faster than using full DFT for the structural relaxation

Quantum Effects: Zero-point Motion

DFT finds the muon sites at the classical potential minima E = 0



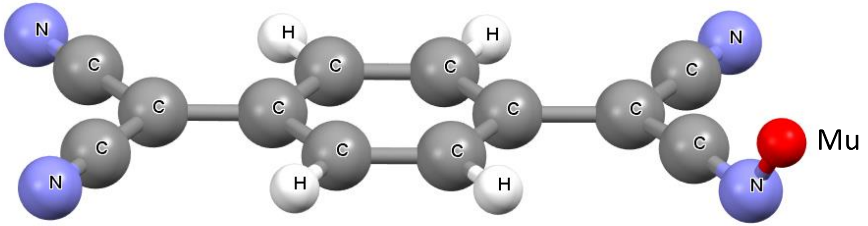
The muon shows strong quantum fluctuations around the classical minimum

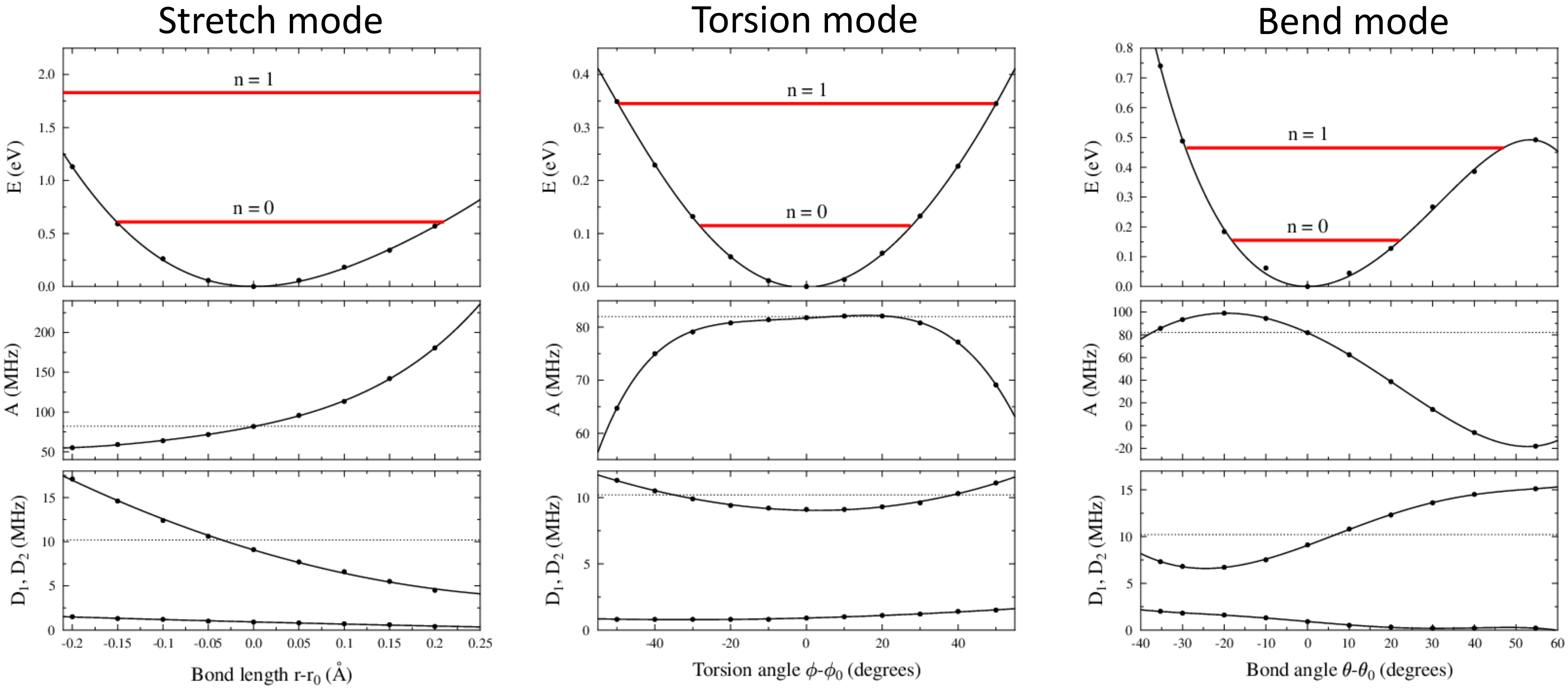
For a quantum harmonic oscillator with frequency ω the quantum zero point energy is $\hbar\omega/2$

Since $\omega \propto m^{-1/2}$ the muon ZPE is 3 times larger than that of a proton in the same potential

Effect of Site ZP Motion on Hyperfine Parameters

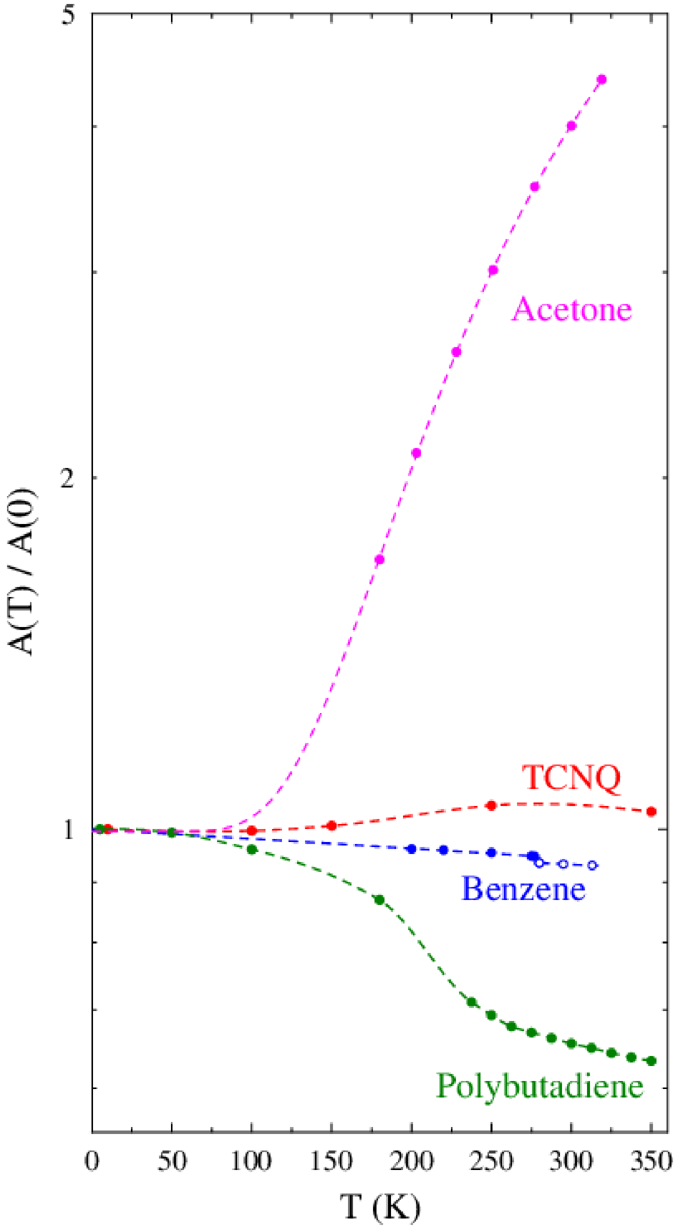
Example of TCNQ



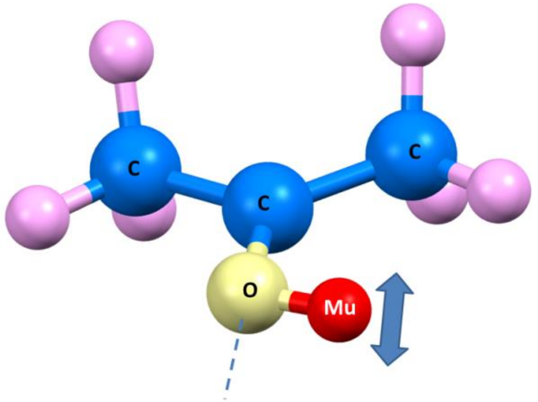


Combined quantum factor from the three modes: 1.10 for A and 1.15 for D_1

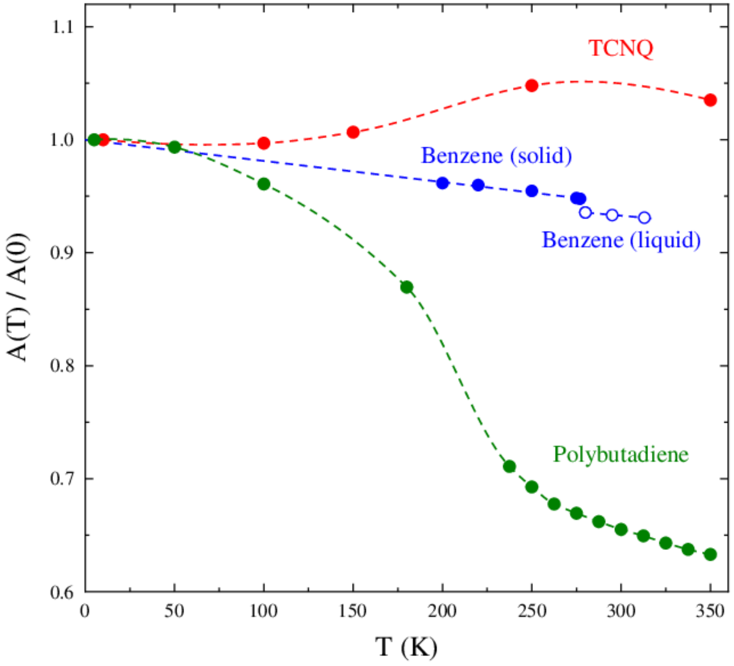
Thermal Effects



Acetone

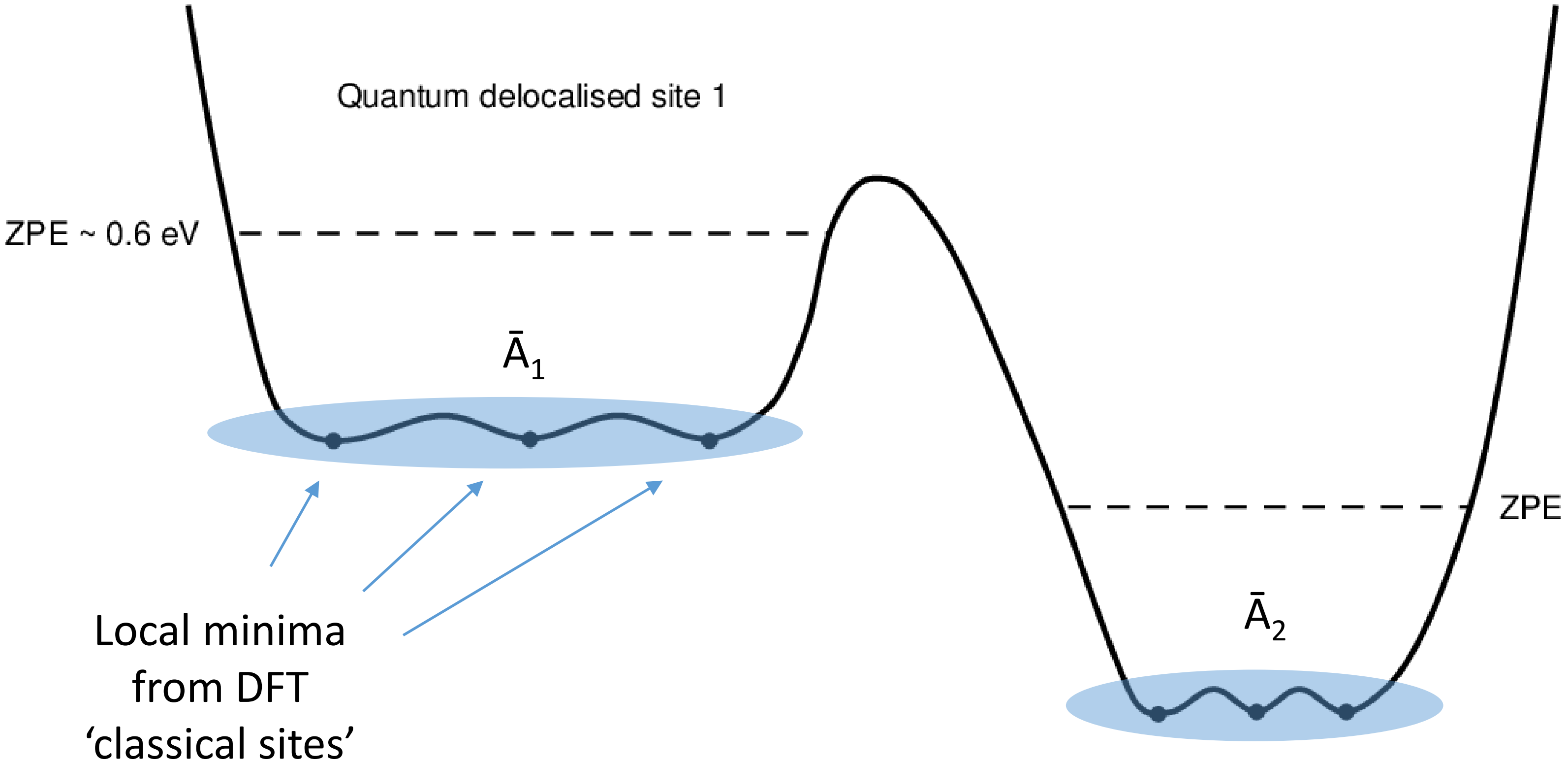


The hyperfine coupling A is strongly dependent on the orientation of the O-Mu bond compared to the C plane



Quantum Delocalisation between Sites

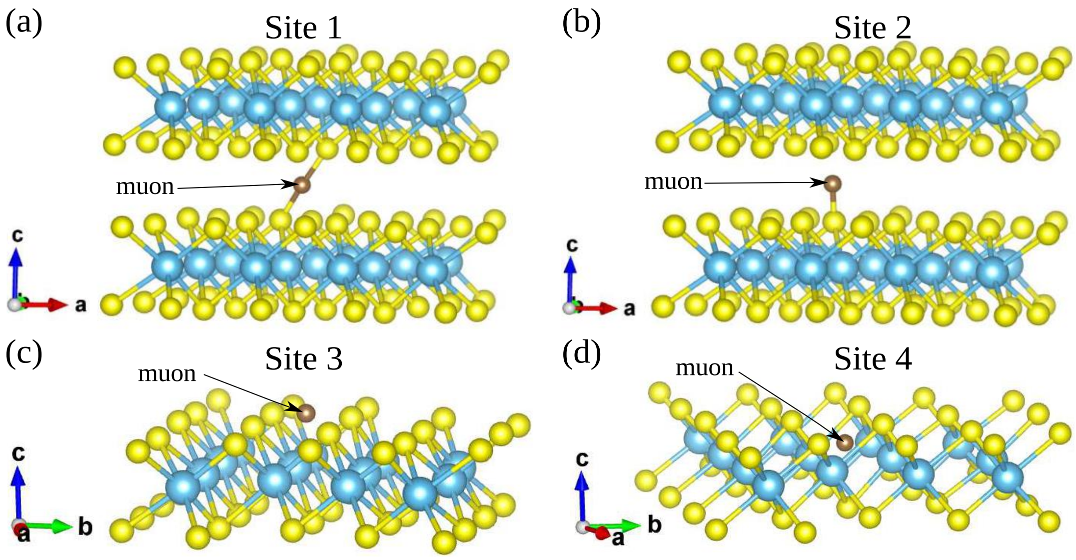
Not just local site quantum correction to consider, also possibility of longer range quantum motion when ZPE > energy barrier between classical sites

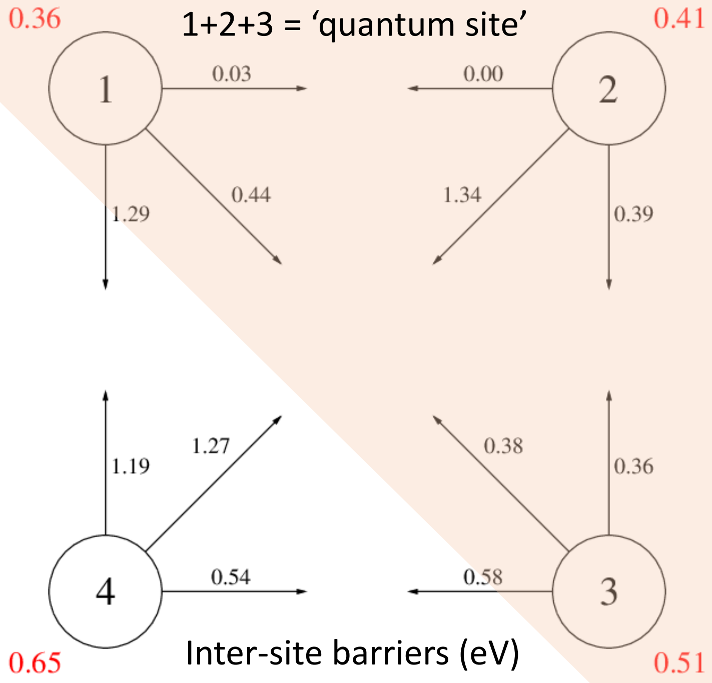


Local minima
from DFT
‘classical sites’

Quantum Delocalisation: Example of 1T-TaS$_2$

CASTEP DFT finds four sites: inter-site barriers and ZP energies are calculated





1+2+3 = ‘quantum site’

Inter-site barriers (eV) versus site ZPE (red)

Site Type	Energy (eV)	Fraction (%)	Average hyperfine coupling (MHz)
1 (interlayer)	0.03	34	6.25
2 (interlayer)	0.06	12	7.60
3 (S layer)	0.09	47	7.70
4 (Ta layer)	0.13	7	-0.92
Site-weighted RMS average			6.61
Average over sites 1-3			7.16

Full ‘quantum site’ is coupled to two TaS$_2$ layers. No *ab* plane delocalisation since barriers are > 1eV

Quantum Tunnelling

For spatially close sites with ZPE only a little lower than the inter-site barrier

Muon Tunnelling versus Proton Tunnelling

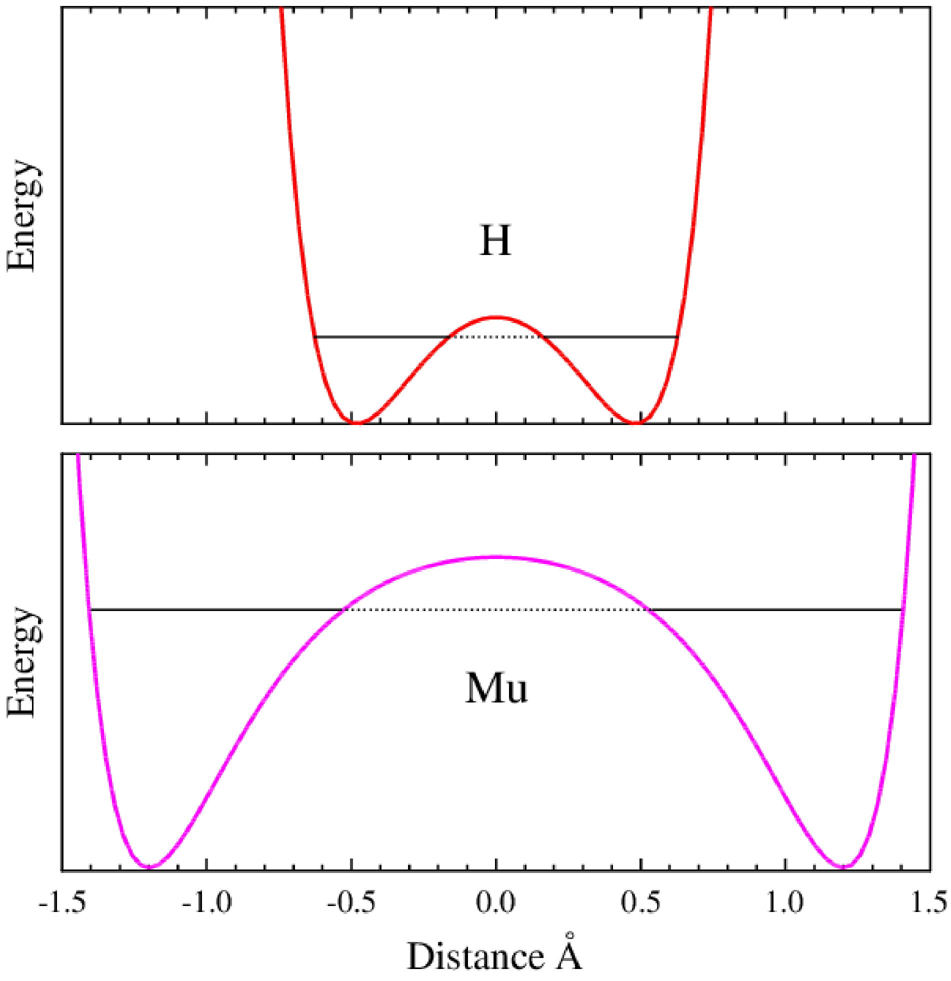
Transmission coefficient for a particle with mass *m* and energy *E* tunnelling through potential barrier *V*(*x*):

$$T(E) = e^{-2\int_{x_1}^{x_2} dx \sqrt{\frac{2m}{\hbar^2}[V(x)-E]}}$$

We have 1/9 mass for Mu versus H:

$\Rightarrow$ larger ZPE (hence smaller *V*(*x*)-*E*)
$\Rightarrow$ faster tunnelling rate
$\Rightarrow$ longer tunnelling range

e.g. ~2.5 Å (Mu) versus ~1 Å (H)



Example: solid benzene and methyl-substituted benzenes

Molecular Dynamics via ALC

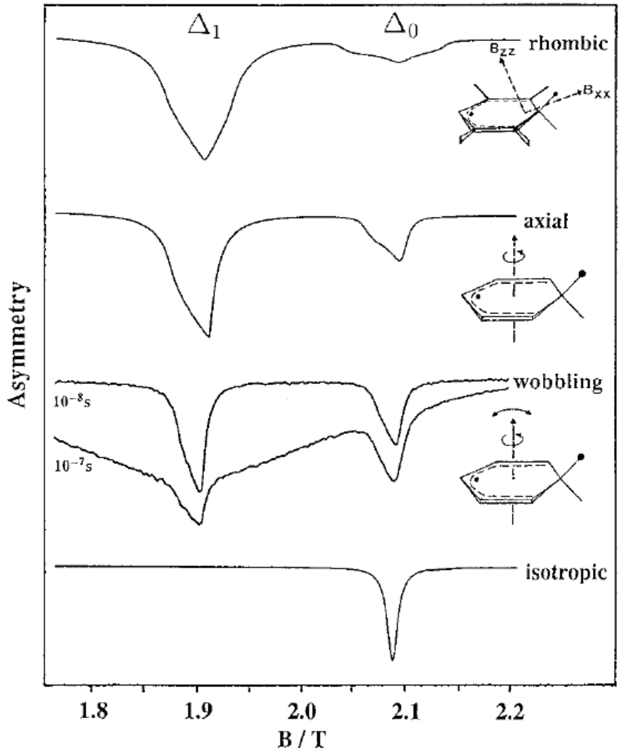
Δ_0 resonances: muon-nuclear flip-flop (the only resonances found in liquids)

Δ_1 resonances: muon flip (usually dominant in solids, need finite dipolar terms)

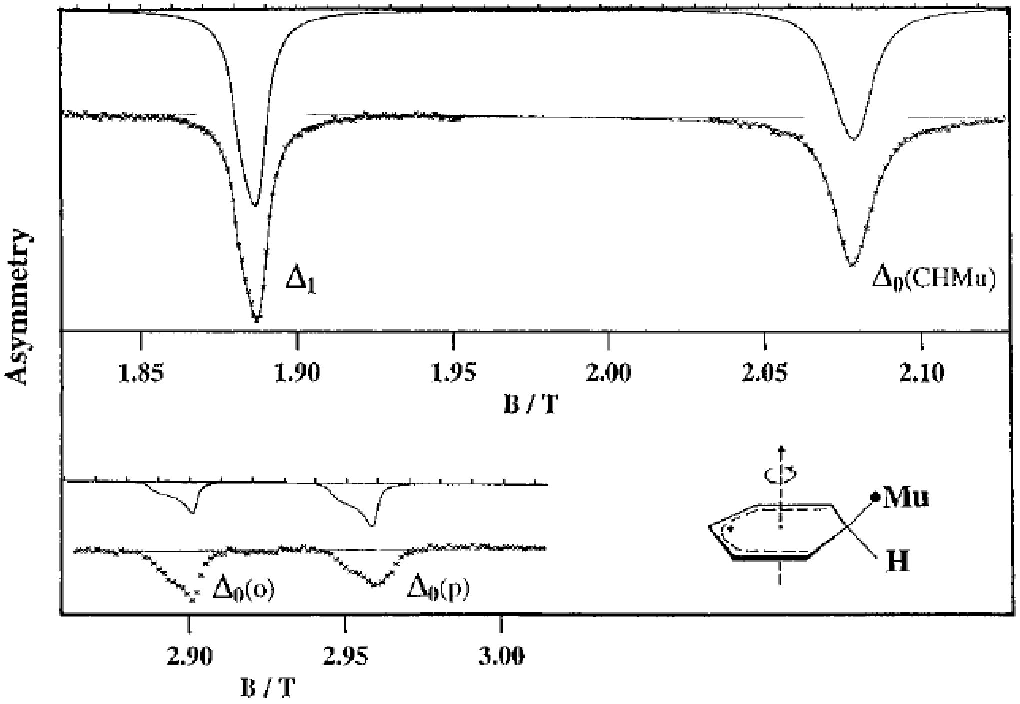
Molecular rotation averages the hyperfine tensor changing in the ALC line shape

e.g. Dynamics of benzene in a zeolite

Calculations



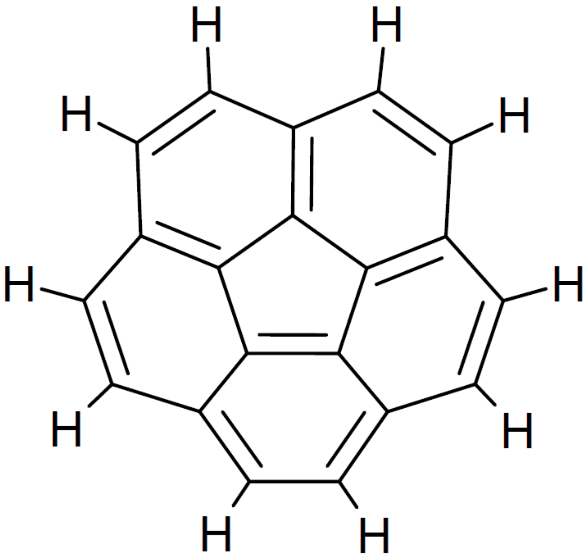
Experimental



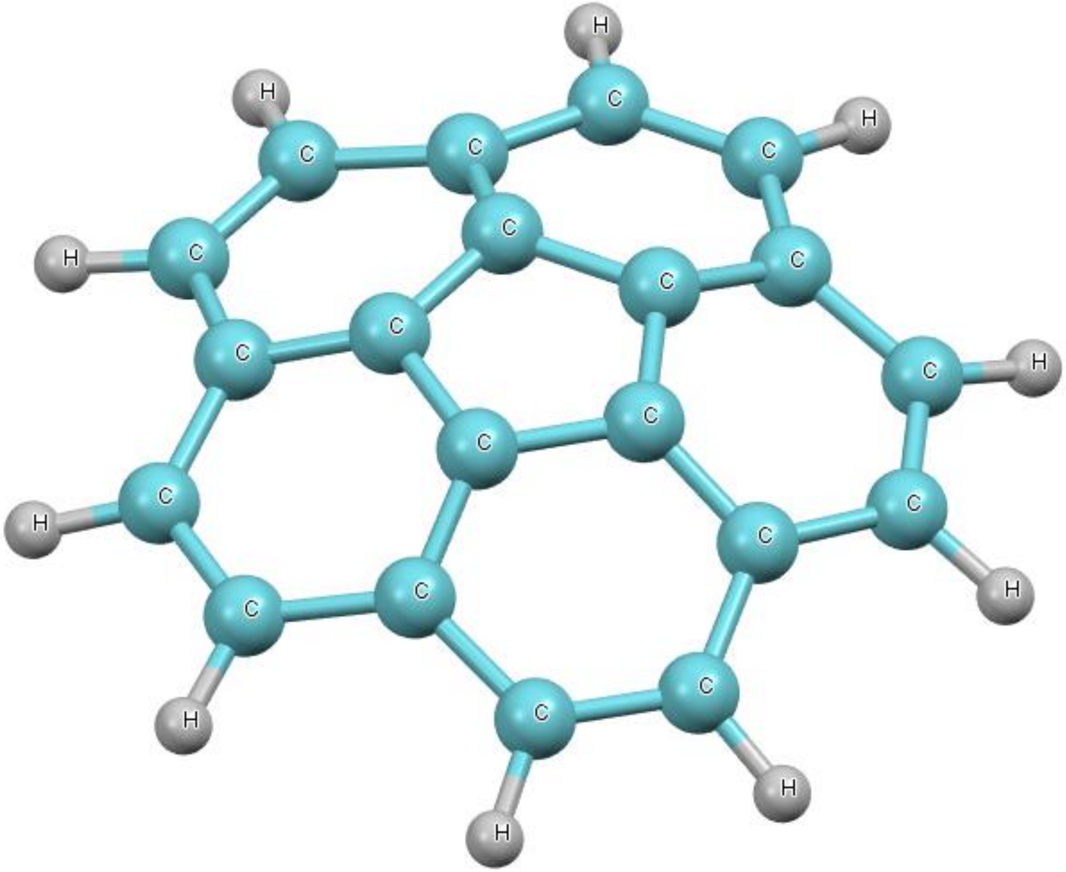
E. Roduner et al, J. Phys. Chem. A 102, 7591 (1998)

Molecular Dynamics via ALC

Corannulene as a potential hydrogen storage medium (Mattia Gaboardi)



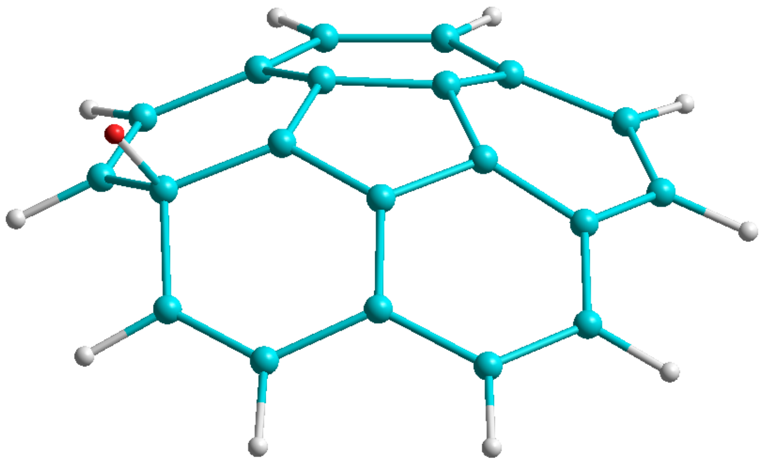
$(C_{20}H_{10})$



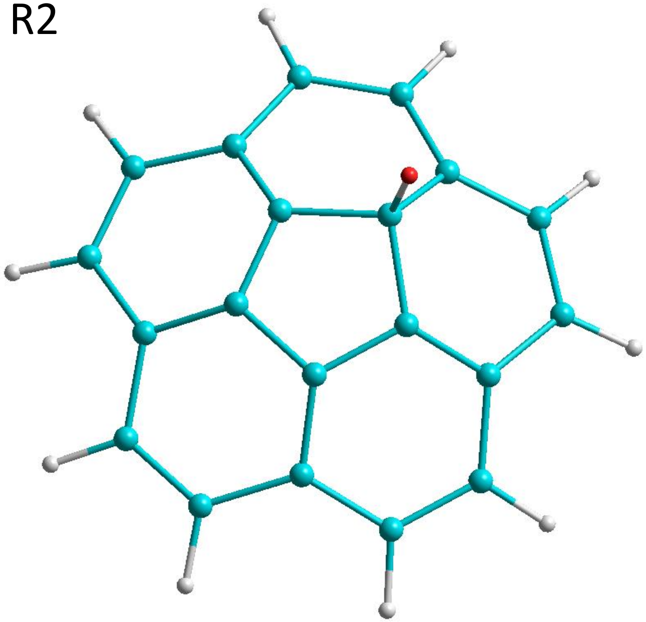
Molecular Dynamics via ALC

Four distinct muon addition sites on the molecule

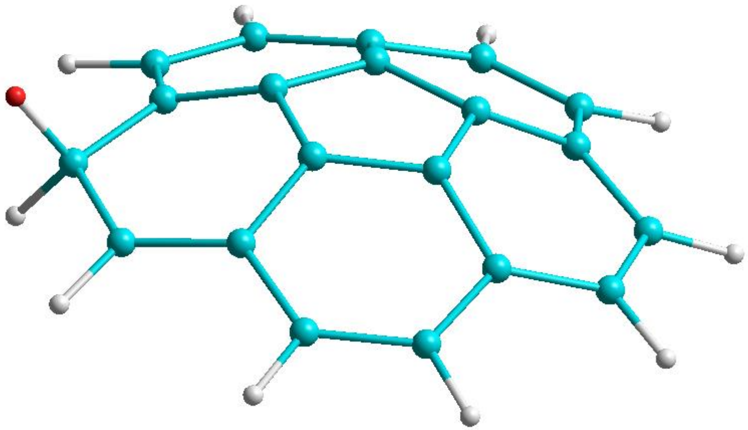
R1



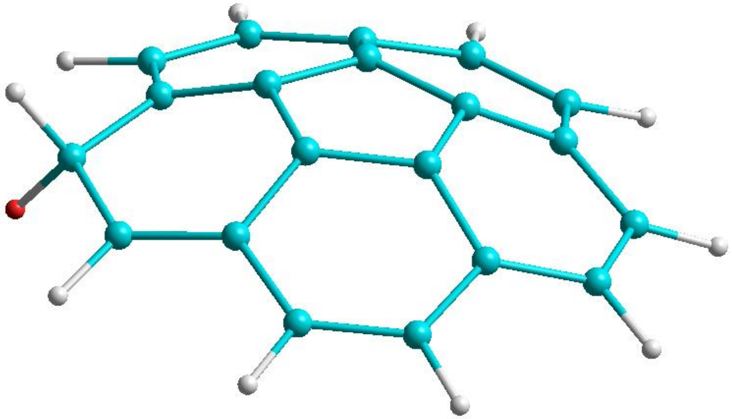
R2



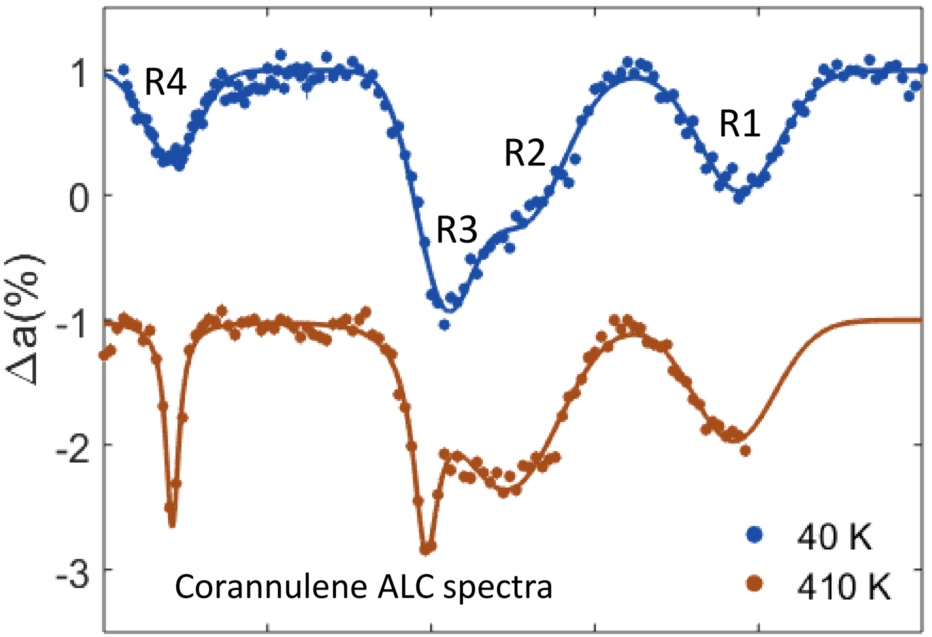
R3

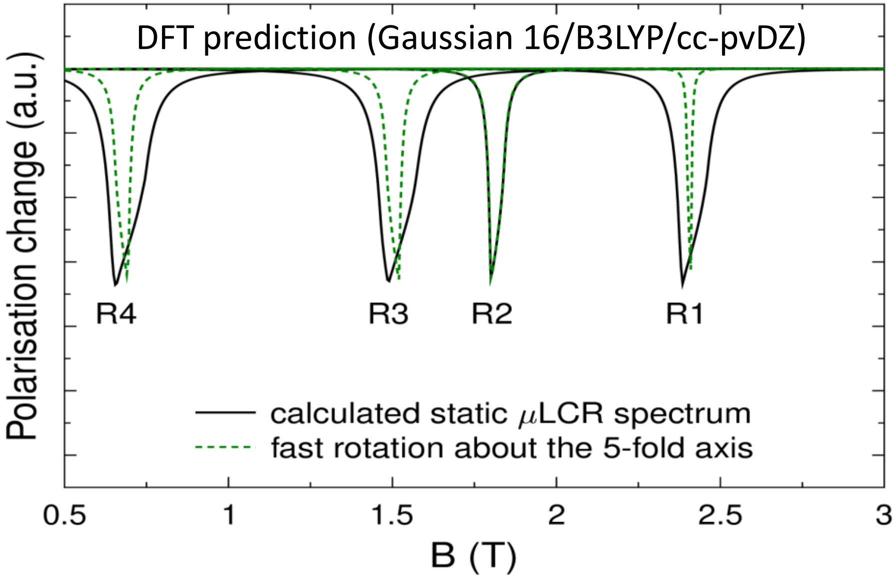


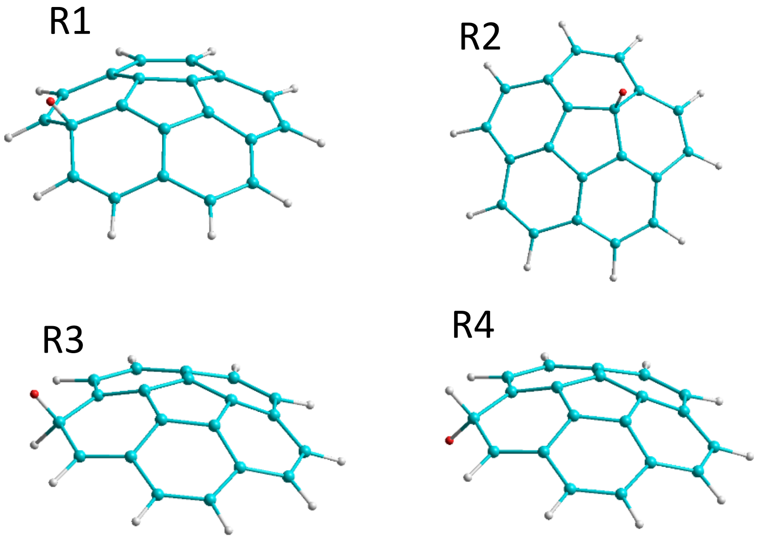
R4



Molecular Dynamics via ALC


Corannulene ALC spectra


DFT prediction (Gaussian 16/B3LYP/cc-pvDZ)



	40 K		410 K		DFT					
	$A_\mu^{(i)}$	Δ	$A_\mu^{(i)}$	Δ	$A_\mu^{(i)}$	D_1	D_2	θ	E	D^{rot}
R1	665(15)	39	660(50)	40	655	14.1	2.5	116	0.67	-2.0
R2	484(53)	41	472(21)	49	494	7.1	0.6	8	0.17	6.9
R3	419(23)	28	404(7)	13	411	17.3	6.5	113	0	-6.7
R4	192(12)	27	193(4)	7	186	17.5	4.0	129	0	-6.7

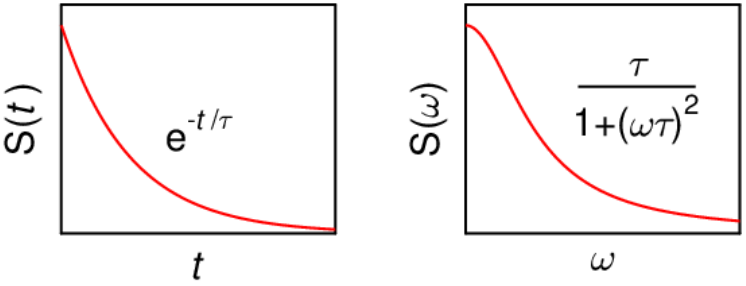
Different Mu/H dynamics at R3 and R4

Electron Dynamics

LF relaxation scales with spectral density function $S(\omega)$ which is the FT of $S(t)$

$$\lambda(B) \propto A^2\, S(\omega), \quad \omega \propto B$$

e.g. localised fluctuations ($d = 0$)



Spectral Density of Fluctuations from Anisotropic Diffusive Motion

$$S(t) = \phi(2D_1 t)\,\phi(2D_2 t)\,\phi(2D_3 t) \quad \text{with } \phi(x) = e^{-x} I_0(x)$$

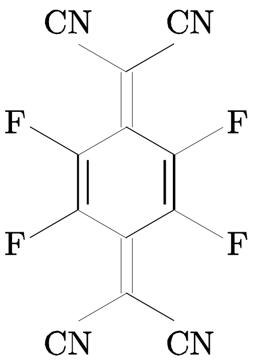
At long t:	$S(t) \propto t^{-m}$	($m=d/2$, d=dimension)
Spectral density:	$S(\omega) \propto \omega^{m-1}$	($0<d<2$, low ω)

$d = 1$	$S(t) \propto t^{-1/2}$	$S(\omega) \propto (D_{1D}\omega)^{-1/2}$
$d = 2$	$S(t) \propto t^{-1}$	$S(\omega) \propto \ln(D_{2D}/\omega)$
$d = 3$	similar to $d = 0$	

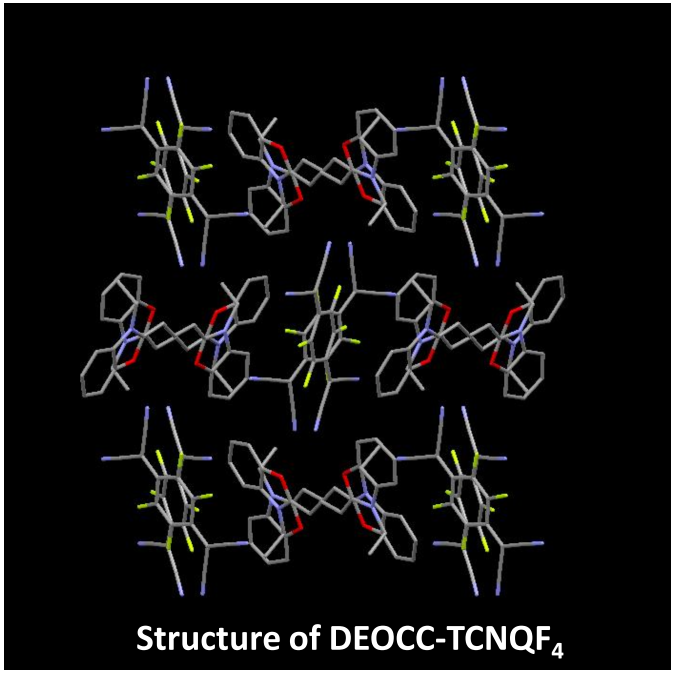
Electron Dynamics in a Spin Chain

An ideal S=1/2 1DHAF: DeOCC-TCNQF$_4$

Molecular radical providing the S=1/2 Heisenberg spins

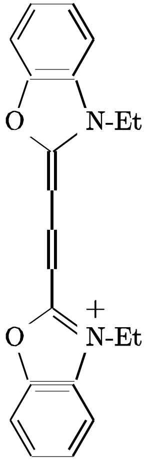


TCNQF$_4$



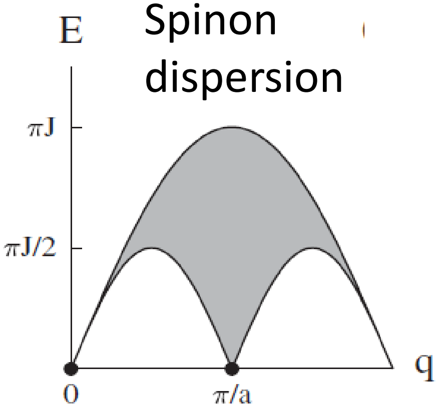
Structure of DEOCC-TCNQF$_4$

Cyanine dye molecule providing the bulky diamagnetic spacers



DEOCC$^+$

Spinon diffusion in a 1D Quantum Magnet:



Spinon dispersion

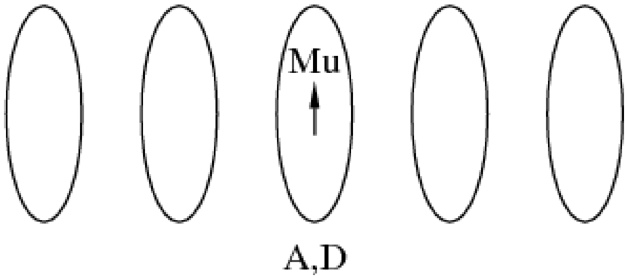
F.L. Pratt et al, Phys. Rev. Lett. 96, 247203 (2006)

Electron Dynamics in Spin Chain

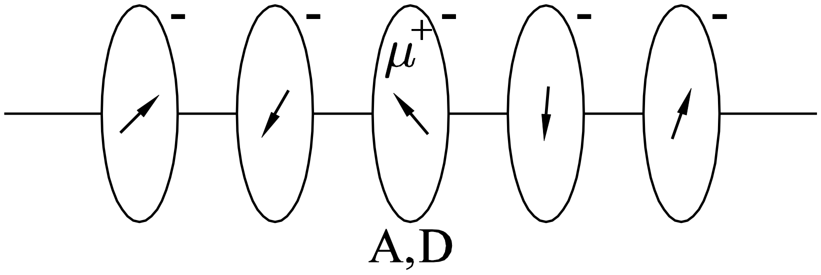
Since $\lambda(B) \propto A^2 S(\omega)$, we need a value for A

ALC on neutral $TFNQF_4$ conveniently gives experimental values for the hyperfine coupling parameters A and D_1

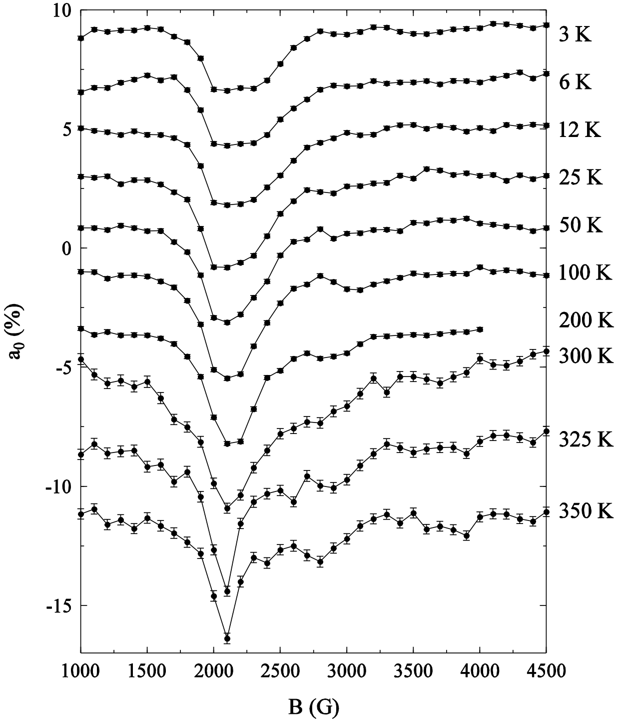
Luckily the muoniated radical in neutral $Mu^{\bullet}$-$TCNQF_4$ (that we can easily measure with ALC)

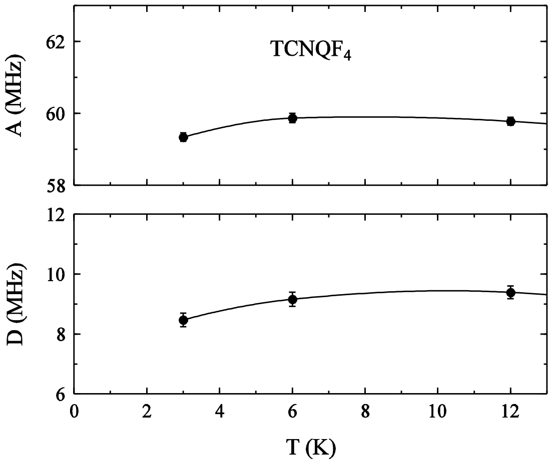


is exactly equivalent to the μ^+ (Mu^+) probe state in our ionic salt: Mu^+-$(TCNQF_4)^-$



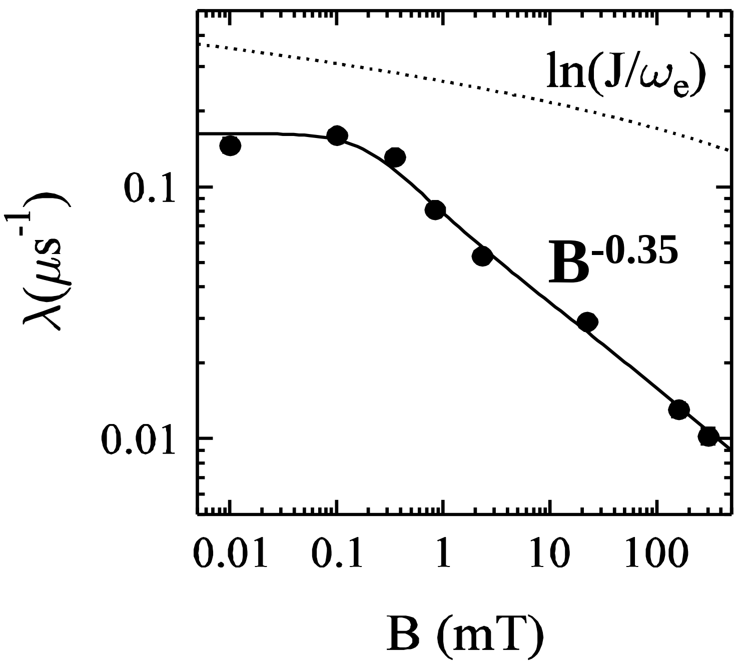
ALC of neutral $TCNQ_4$



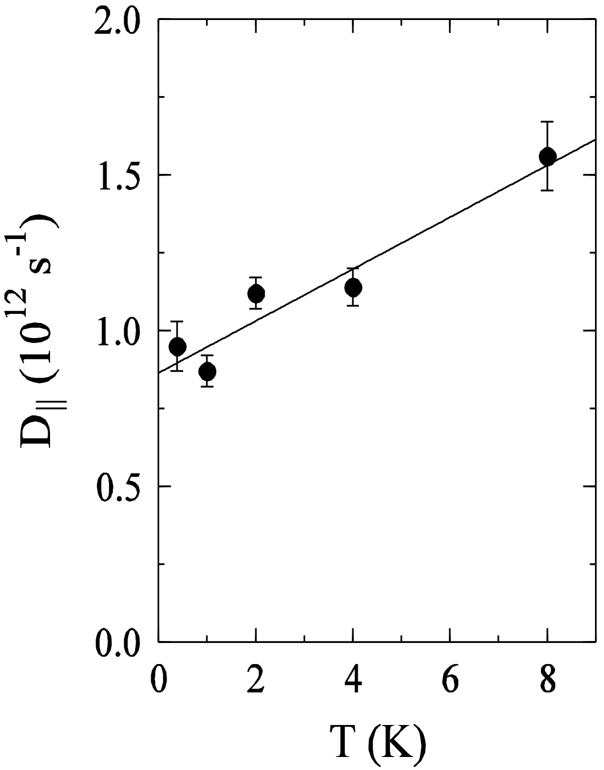


Electron Dynamics in a Spin Chain

LF Relaxation Rate



On-chain Diffusion Rate



N.B. absolute value of $D_{\parallel}$ depends on the *fourth power* of the hyperfine coupling A

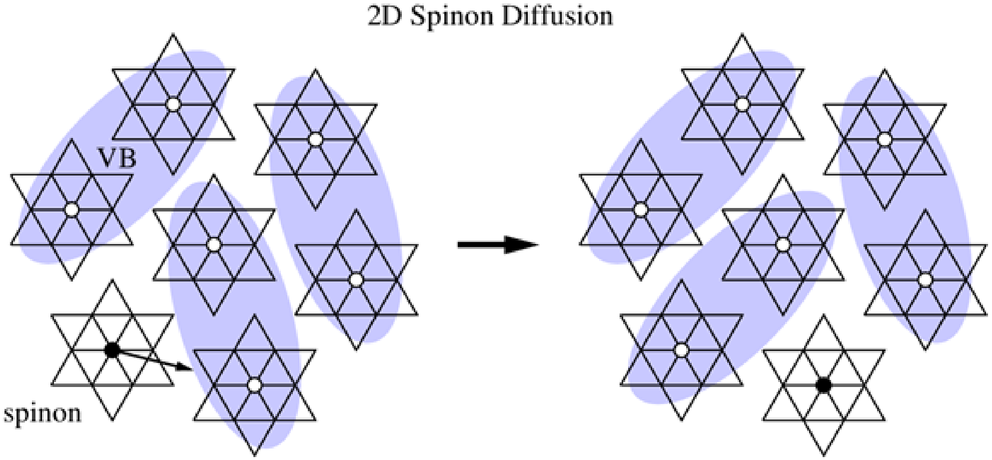
Hopping time $D_{\parallel}^{-1}$ is ~ 1 ps at low T

Compare with:	Spinon transit time $(2/\pi)/J$	~ 0.3 ps
	Classical diffusion time $(2/\pi)^{1/2}/J$	~ 0.3 ps

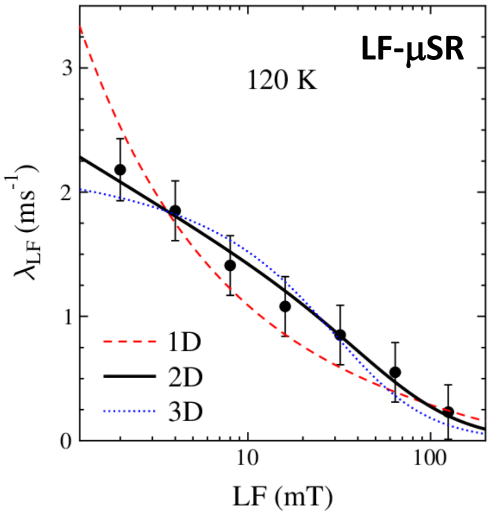
Electron Dynamics in a Layered Quantum Magnet

2D Quantum Magnet: spinon diffusion in the spin liquid 1T-TaS_2

Star-of-David $S = 1/2$ ‘molecule’ formed by CDW distortion



2D spinon diffusion from LF-μSR



No related ALC resonances are available here to determine the HFC

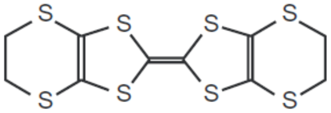
We have to rely on the DFT calculations alone to calibrate the measurements

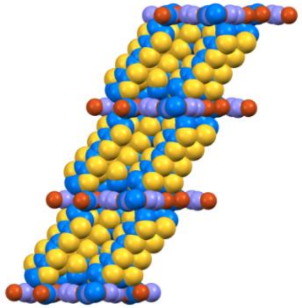
The values estimated from DFT site analysis in this case are A = 7(1) MHz and $D_1 = D_2 = 0$

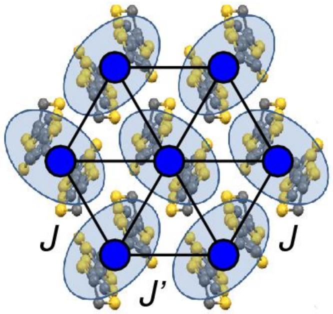
Static Electronic Order

κ-$(ET)_2X$ family: magnets, superconductors and spin liquids

ET molecule:

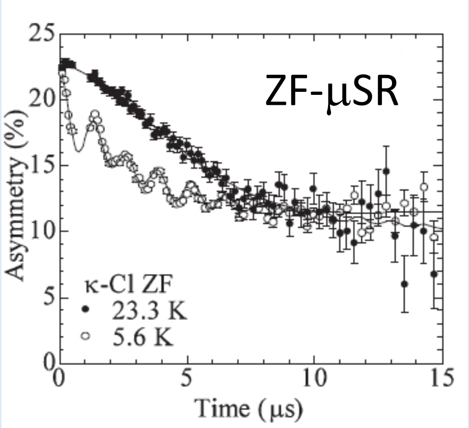


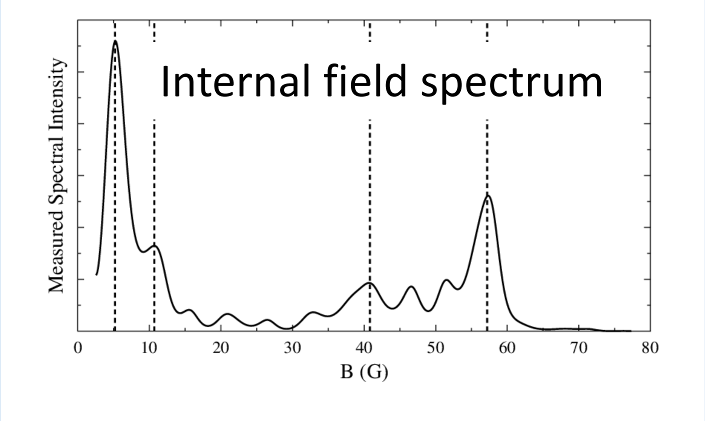




***J* = 250 K**

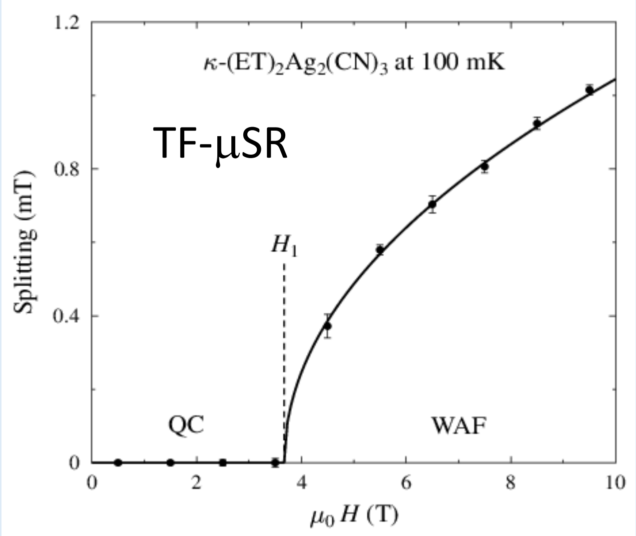
Antiferromagnet (X=Cu$[N(CN)_2]$Cl)

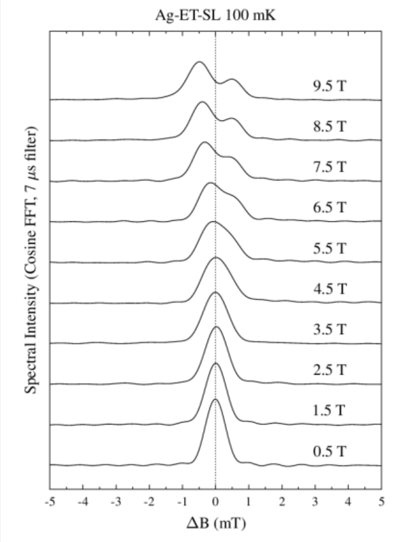




M. Ito et al, JPSJ 84,053703 (2015)

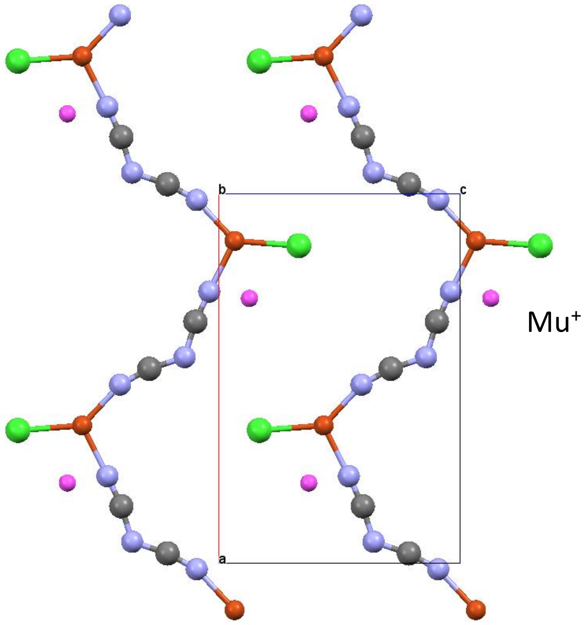
Quantum Spin Liquid (X=$Cu_2(CN)_3$ and X=$Ag_2(CN)_3$)



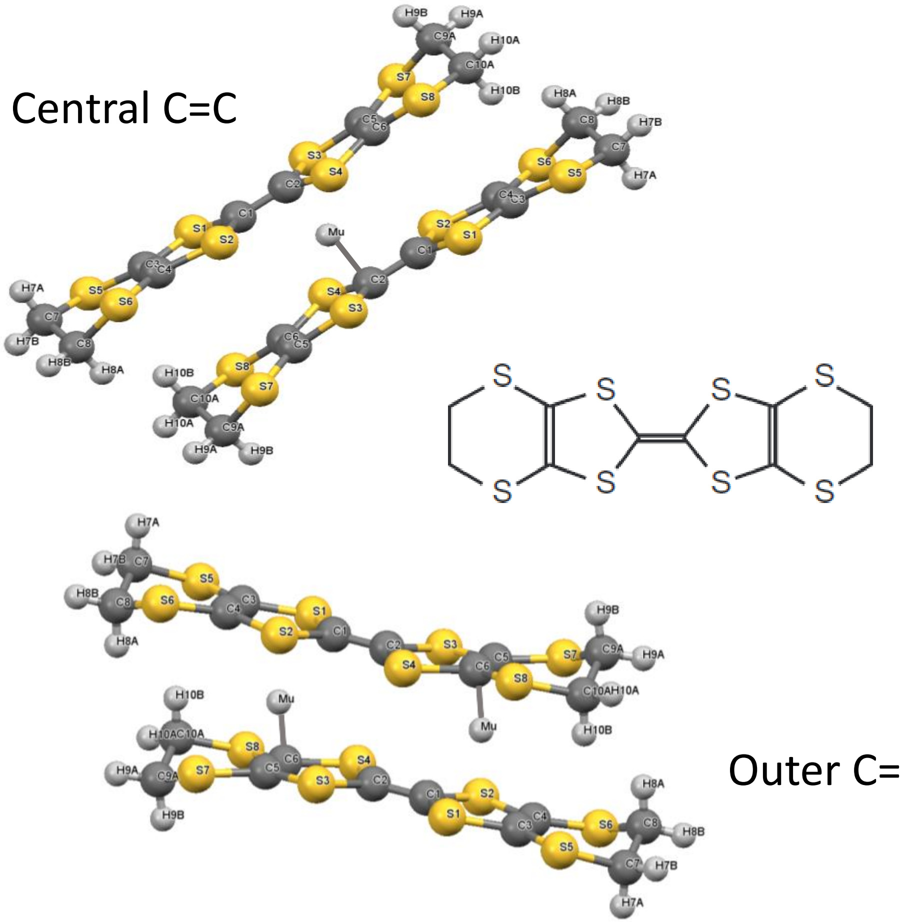


Static Electronic Order

CASTEP plane-wave DFT for the AF case of X=CuN(CN)$_2$Cl



Mu⁺ (bare μ^+) sites located in the anion layer (diamagnetic probe states)



Central C=C

Outer C=C

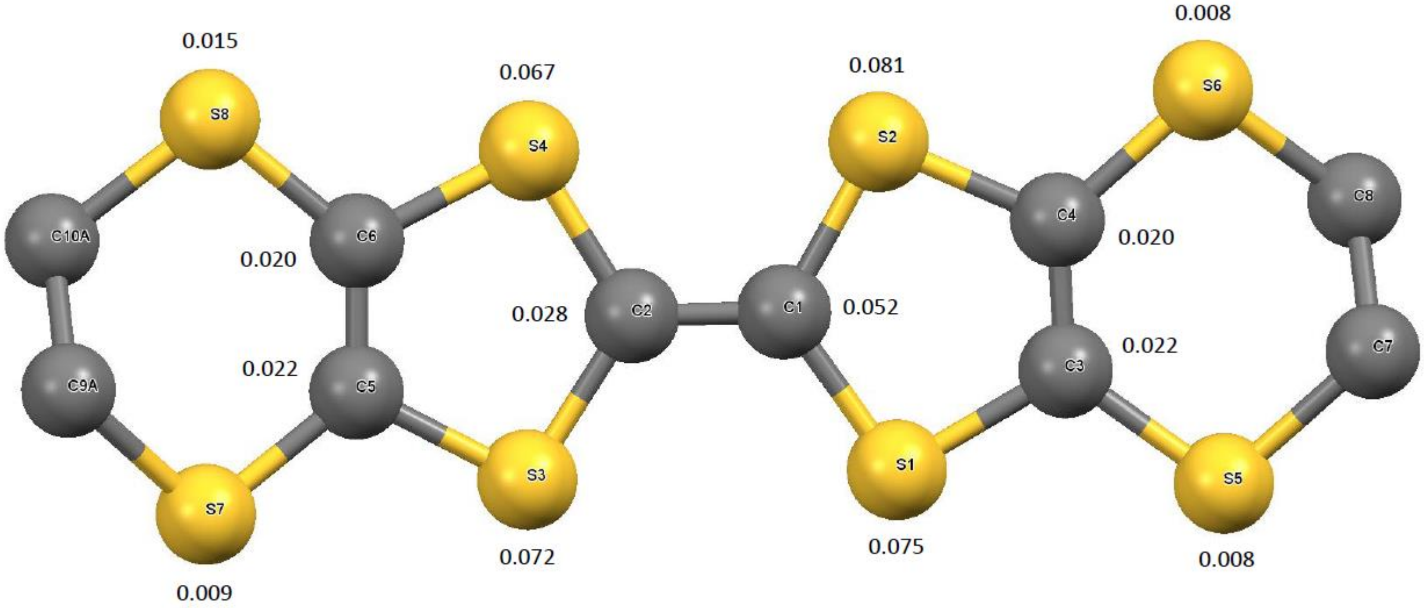
Mu addition sites in the ET layer

$(\mathrm{ET})_2^{\bullet +}$ + $\mathrm{Mu}^{\bullet}$ $\rightarrow$ $(\mathrm{ET})_2\mathrm{Mu}$ (singlet)

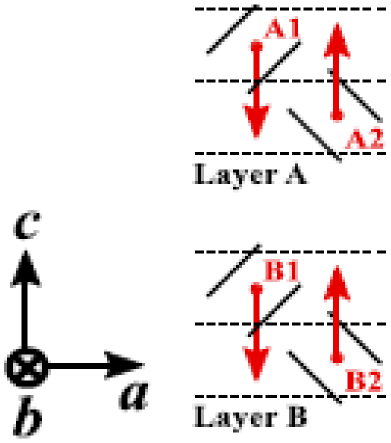
(diamagnetic probe states)

Static Electronic Order

The spin distribution calculated for a single $(ET)_2^+$ dimer using Gaussian DFT (B3LYP/cc-pVDZ) shows significant spin on 14 sites



Spin structure of the ordered state in ZF with the magnetic cell containing 8 ET molecules

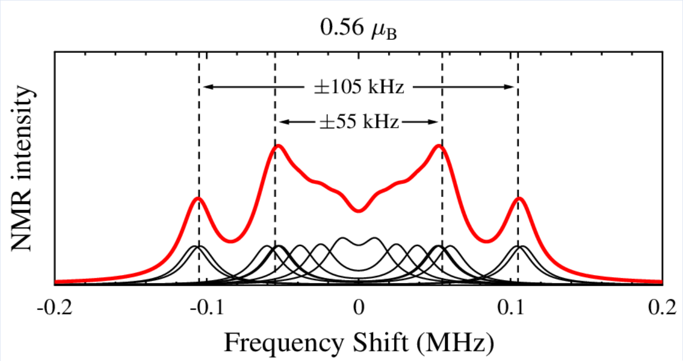


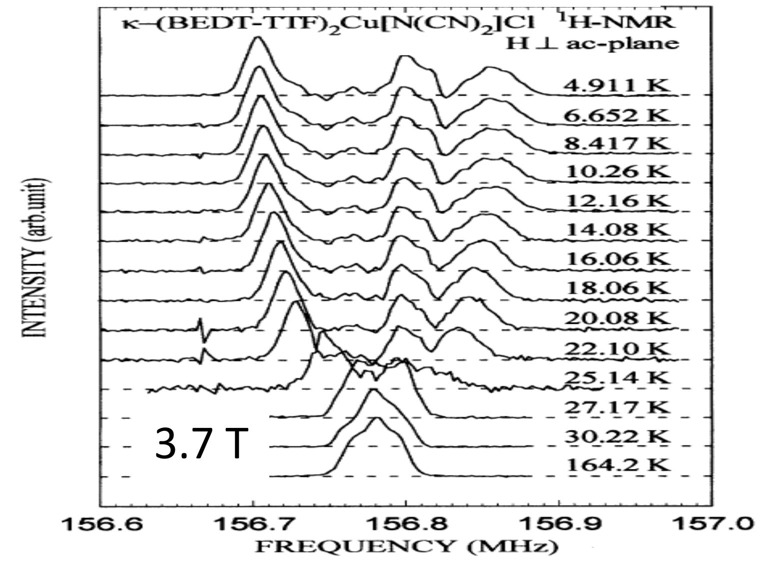
Dipolar field calculation requires 14×8 = 112 spin elements in the magnetic cell for collinear order and 336 spin elements for the 120° structure (the DipoleCalc program can be used here)

Static Electronic Order

Proton NMR

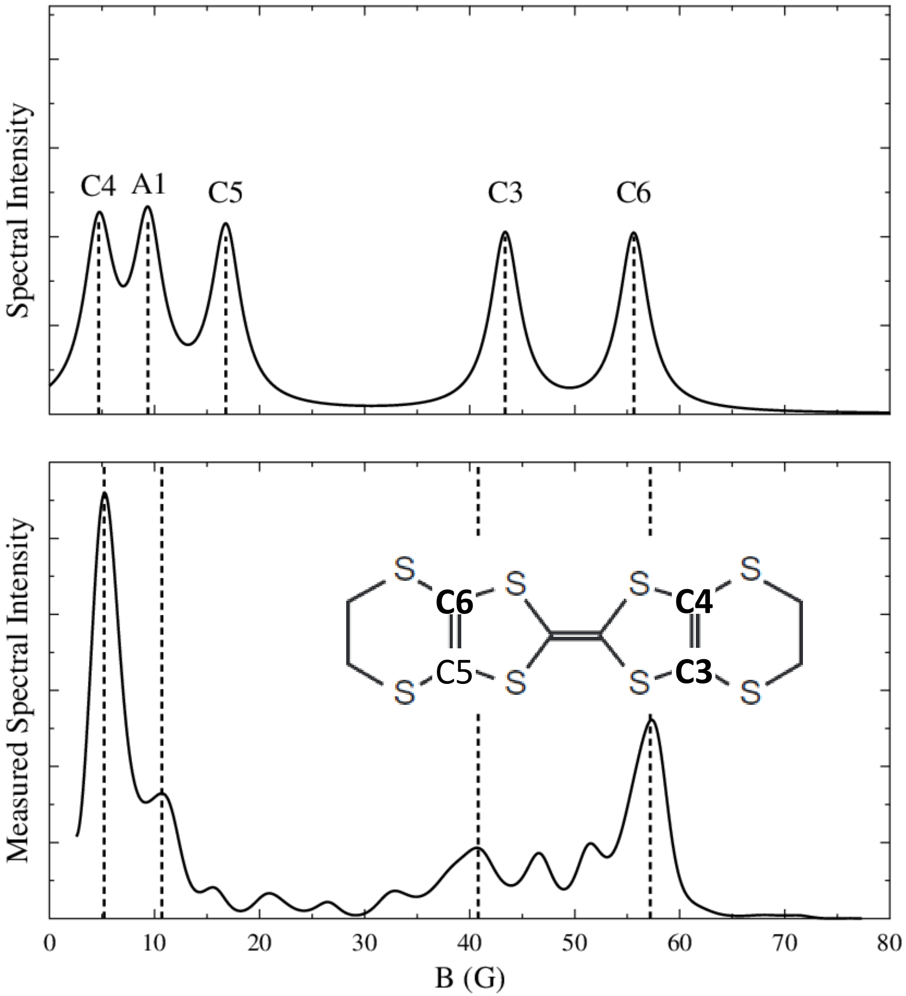
Testing the Gaussian-DFT spin distribution against the published ^{1}H-NMR spectrum





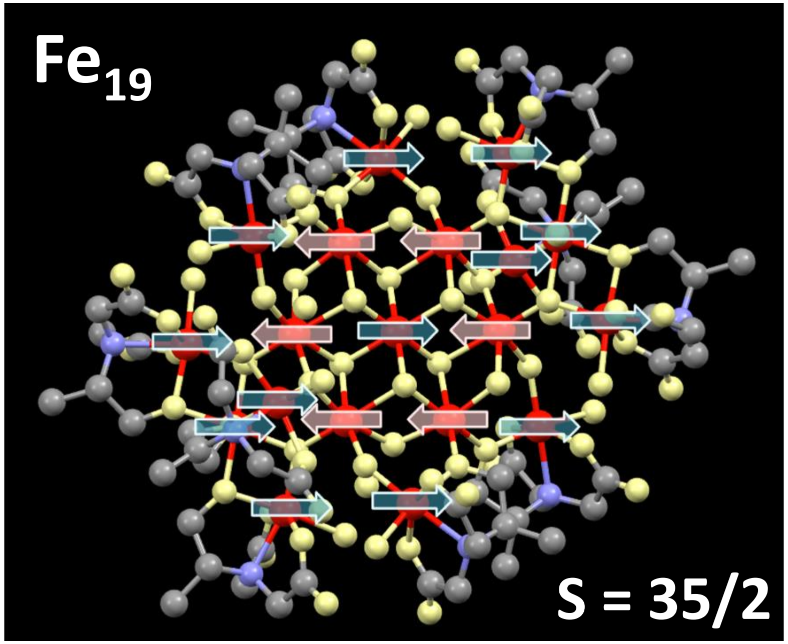
K. Miyagawa et al, Phys. Rev. Lett. 75, 1174 (1995)

ZF μSR



Calculated internal fields for *m* = 0.68 μ_B match well to the spectrum obtained from the measured ZF-μSR data with addition at *outer C=C sites* plus an *anion layer site*

Large Systems: Complex Unit Cell



Fe_{19} nanodisc molecular magnet (T_N = 1.2 K)

Magnetic cell has 1580 atoms and 78 Fe spins

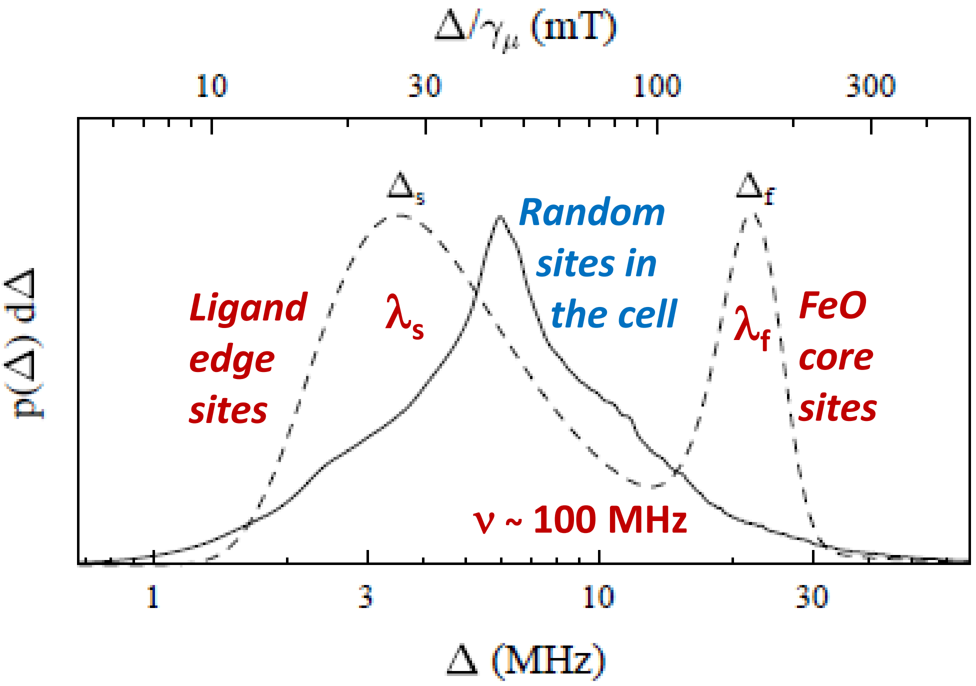
Much too large for the usual discrete sites approach!

Switch to a site distribution approach

Random sites calculation for reference

ZF-μSR sees a two-lorentzian relaxation: local coupling Δ has bimodal distribution

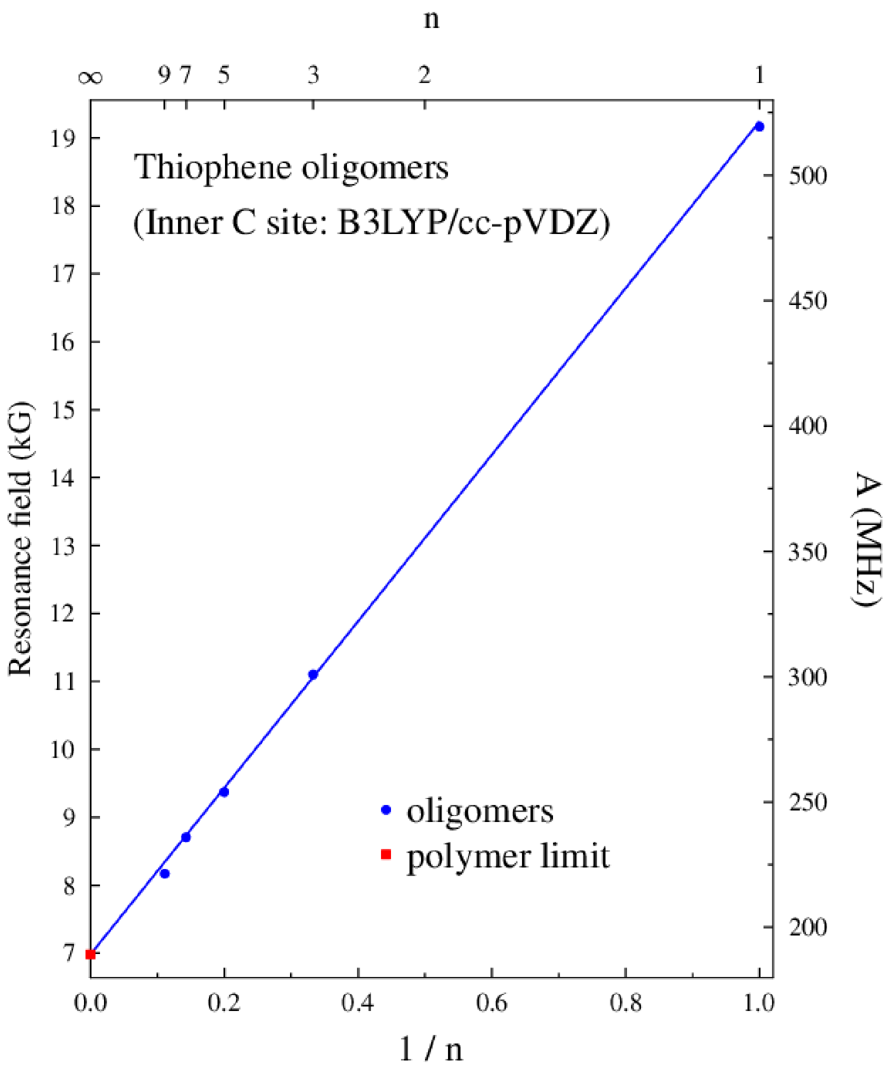
The two distribution peaks are assigned to ligand edge sites and FeO core sites



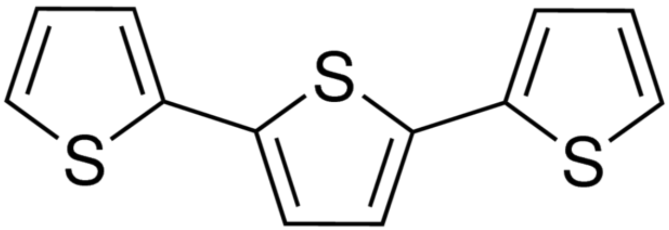
F.L. Pratt et al, Phys. Rev. B 89, 144420 (2014)

Large Systems: Polythiophene via Oligomers

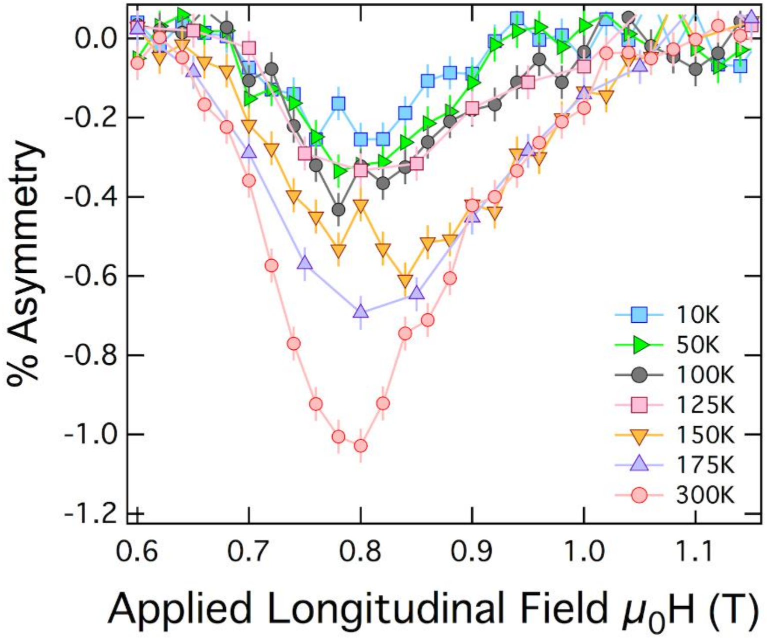
Gaussian DFT prediction of Δ_1 ALC



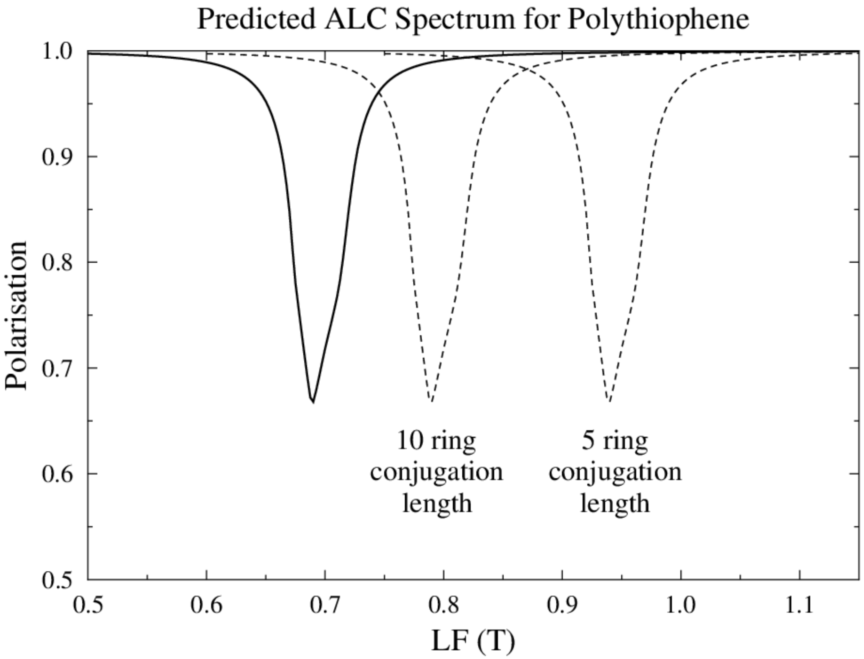
thiophene oligomer (n = 3)

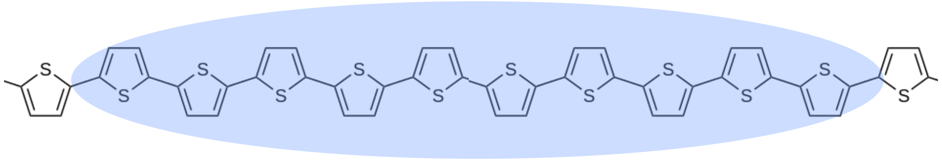


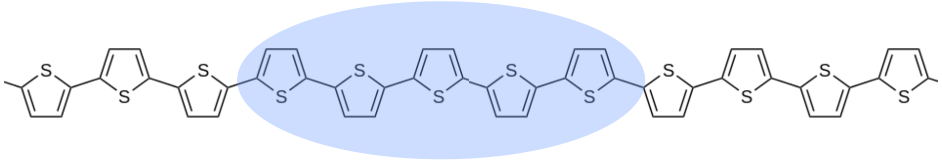
Poly-3-hexyl-thiophene (RR)

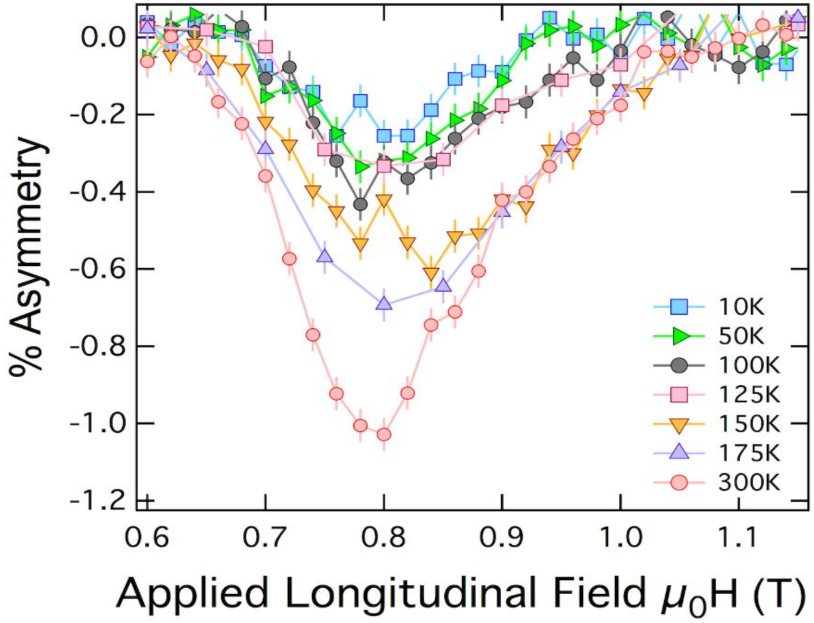


Effect of Disorder









The broad ALC spectrum shows the range of π-electron conjugation lengths in the polymer

Larger Systems: Possible Future Directions

Linear-scaling methods:	N-scaling rather than N^3-scaling e.g. the ONETEP project (based on intelligent truncation of overlap integrals and efficient use of sparse matrix methods)
Multiscale methods:	Use full DFT in a local region around the muon Use simpler methods such as Molecular Mechanics in the more distant regions

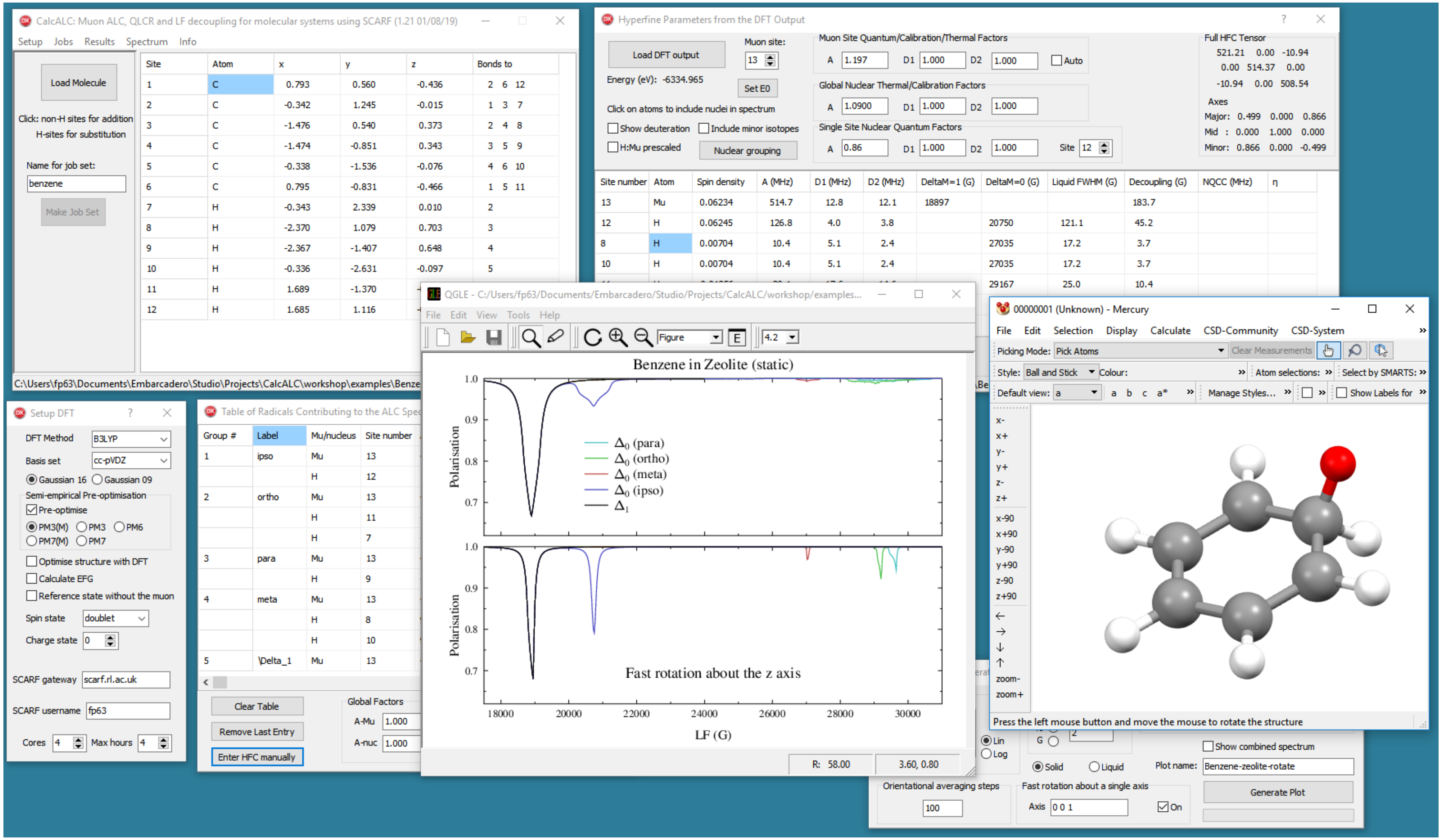
Status Summary

- Rapid progress has been made recently in site calculation methods
- Efficient and practical methods for simulating ALC spectra in molecular systems
- Both single molecules and periodic crystal systems can be covered
- Methods developed for dealing with the quantum delocalisation effects
- Various user tools are now available to assist with managing the site calculations
- Technique development is still required for some areas

Workshop (N): CalcALC

Takes a molecule and calculates muoniated radical states and their corresponding ALC spectra

(uses Gaussian DFT on SCARF for the calculation, can also work with results from CASTEP, the ALC spectra are calculated using the Python library of James Lord's Quantum program)



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

Name for job set: benzene

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		
12	H	1.685	1.116		

C:\Users\fp63\Documents\Embarcadero\Studio\Projects\CalcALC\workshop\examples\Benze

Muon site: 13

Energy (eV): -6334.965

Click on atoms to include nuclei in spectrum

☐ Show deuteration ☐ Include minor isotopes

☐ H:Mu prescaled

Muon Site Quantum/Calibration/Thermal Factors
A 1.197 D1 1.000 D2 1.000 ☐ Auto

Global Nuclear Thermal/Calibration Factors
A 1.0900 D1 1.000 D2 1.000

Single Site Nuclear Quantum Factors
A 0.86 D1 1.000 D2 1.000 Site 12

Full HFC Tensor
521.21 0.00 -10.94
0.00 514.37 0.00
-10.94 0.00 508.54

Axes
Major: 0.499 0.000 0.866
Mid : 0.000 1.000 0.000
Minor: 0.866 0.000 -0.499

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	0.06234	514.7	12.8	12.1	18897			183.7		
12	H	0.06245	126.8	4.0	3.8		20750	121.1	45.2		
8	H	0.00704	10.4	5.1	2.4		27035	17.2	3.7		
10	H	0.00704	10.4	5.1	2.4		27035	17.2	3.7		
							29167	25.0	10.4		

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: scarf.rl.ac.uk

SCARF username: fp63

Cores: 4 Max hours: 4

Group #	Label	Mu/nucleus	Site number
1	ipso	Mu	13
		H	12
2	ortho	Mu	13
		H	11
		H	7
3	para	Mu	13
		H	9
4	meta	Mu	13
		H	8
		H	10
5	\Delta_1	Mu	13

Global Factors
A-Mu 1.000
A-nuc 1.000

Press the left mouse button and move the mouse to rotate the structure

● Lin ○ Log

G ○ 2

● Solid ○ Liquid

☐ Show combined spectrum

Plot name: Benzene-zeolite-rotate

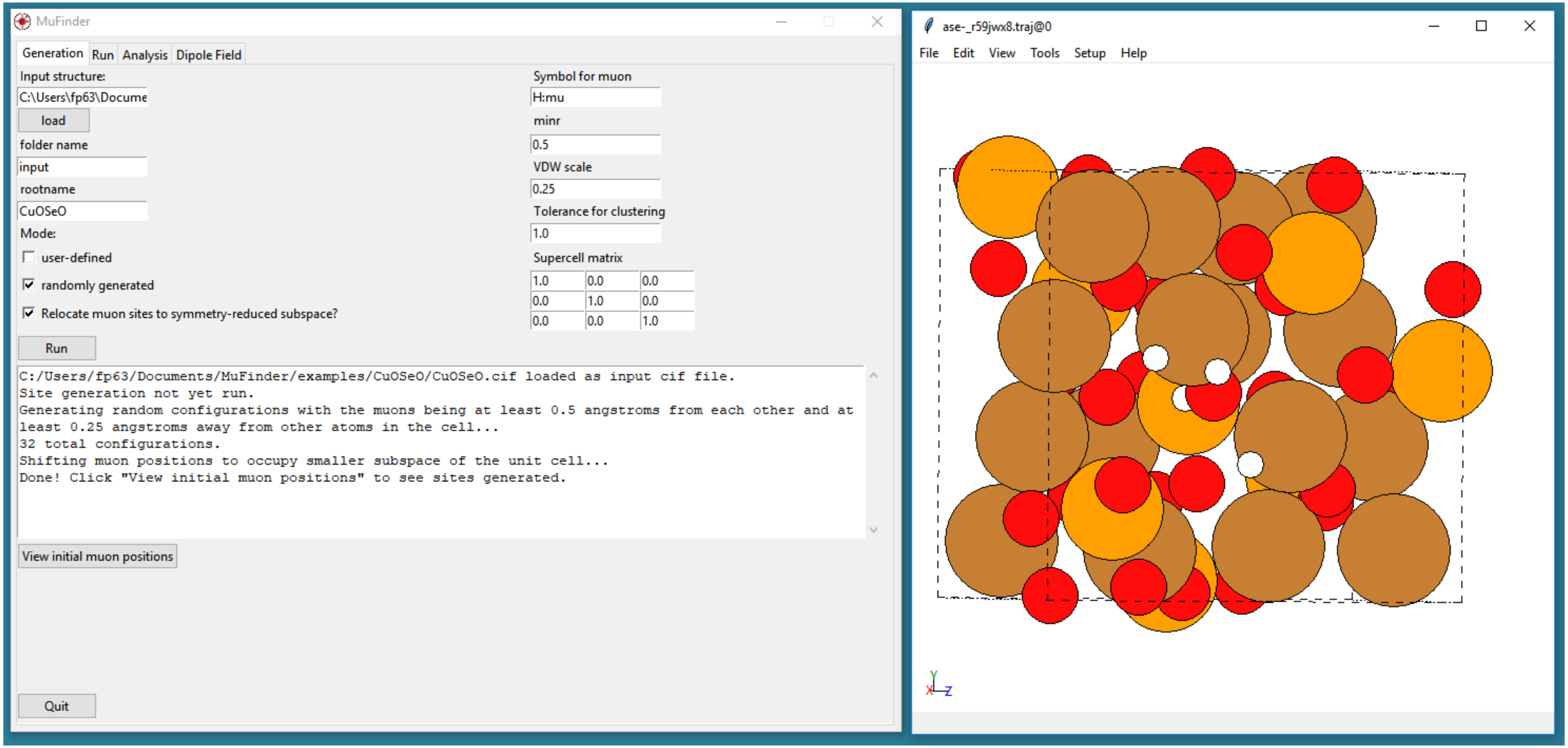
Orientational averaging steps: 100

Fast rotation about a single axis
Axis 0 0 1 ☑ On

Workshop (N): MuFinder

Takes a crystal structure and calculates a set of stable muon sites using CASTEP on SCARF

Explores the dipolar fields at these sites for a magnetically ordered state



Input structure: C:\Users\fp63\Docume

folder name: input

rootname: CuOSeO

Mode:

☐ user-defined

☑ randomly generated

☑ Relocate muon sites to symmetry-reduced subspace?

Symbol for muon: H:mu

minr: 0.5

VDW scale: 0.25

Tolerance for clustering: 1.0

Supercell matrix

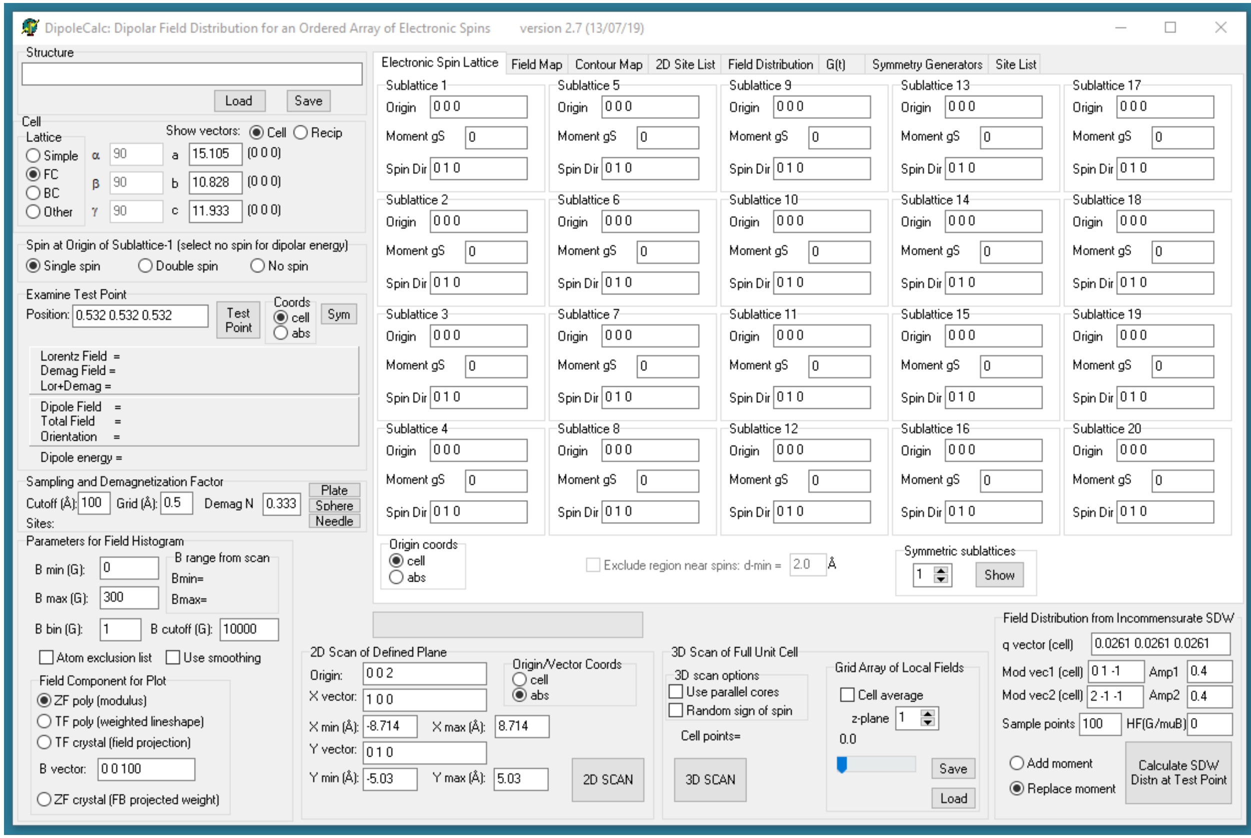
1.0	0.0	0.0
0.0	1.0	0.0
0.0	0.0	1.0

```
C:/Users/fp63/Documents/MuFinder/examples/CuOSeO/CuOSeO.cif loaded as input cif file.
Site generation not yet run.
Generating random configurations with the muons being at least 0.5 angstroms from each other and at
least 0.25 angstroms away from other atoms in the cell...
32 total configurations.
Shifting muon positions to occupy smaller subspace of the unit cell...
Done! Click "View initial muon positions" to see sites generated.
```

Workshop (N): DipoleCalc

Takes the sites determined by DFT and explores the dipolar fields in ordered magnetic states

(includes features developed for treating muons in complex molecular magnetic systems and also has the ability to simulate incommensurate SDW systems such as MnSi)



DipoleCalc: Dipolar Field Distribution for an Ordered Array of Electronic Spins version 2.7 (13/07/19)

Cell
Lattice: ○ Simple ● FC ○ BC ○ Other
Show vectors: ● Cell ○ Recip
α 90, β 90, γ 90
a 15.105 (0 0 0)
b 10.828 (0 0 0)
c 11.933 (0 0 0)

Spin at Origin of Sublattice-1 (select no spin for dipolar energy): ● Single spin ○ Double spin ○ No spin

Examine Test Point
Position: 0.532 0.532 0.532
Coords: ● cell ○ abs

Lorentz Field =
Demag Field =
Lor+Demag =
Dipole Field =
Total Field =
Orientation =
Dipole energy =

Sampling and Demagnetization Factor
Cutoff (Å): 100 Grid (Å): 0.5 Demag N 0.333
Sites:

Parameters for Field Histogram
B min (G): 0
B max (G): 300
B bin (G): 1
B cutoff (G): 10000
B range from scan: Bmin= Bmax=
☐ Atom exclusion list ☐ Use smoothing

Field Component for Plot
● ZF poly (modulus)
○ TF poly (weighted lineshape)
○ TF crystal (field projection)
B vector: 0 0 100
○ ZF crystal (FB projected weight)

Sublattice	Origin	Moment gS	Spin Dir
1	0 0 0	0	0 1 0
2	0 0 0	0	0 1 0
3	0 0 0	0	0 1 0
4	0 0 0	0	0 1 0
5	0 0 0	0	0 1 0
6	0 0 0	0	0 1 0
7	0 0 0	0	0 1 0
8	0 0 0	0	0 1 0
9	0 0 0	0	0 1 0
10	0 0 0	0	0 1 0
11	0 0 0	0	0 1 0
12	0 0 0	0	0 1 0
13	0 0 0	0	0 1 0
14	0 0 0	0	0 1 0
15	0 0 0	0	0 1 0
16	0 0 0	0	0 1 0
17	0 0 0	0	0 1 0
18	0 0 0	0	0 1 0
19	0 0 0	0	0 1 0
20	0 0 0	0	0 1 0

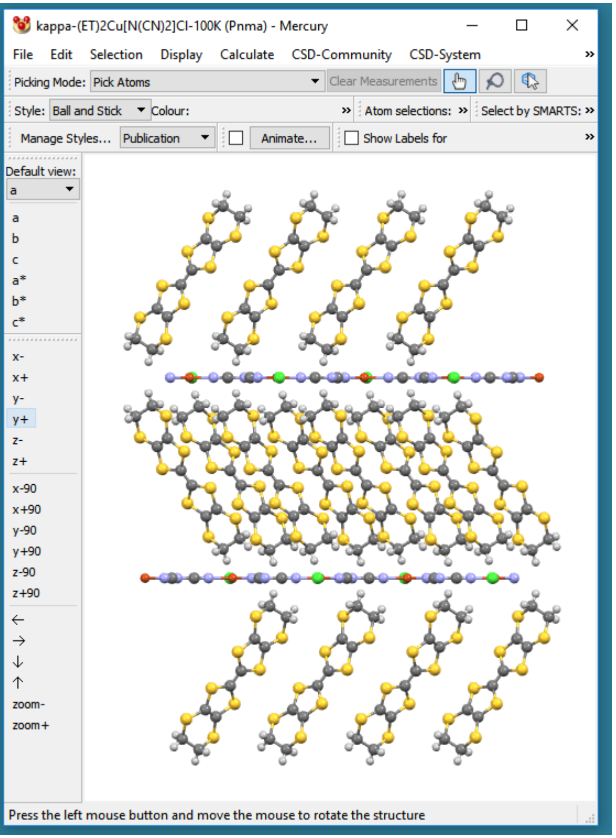
Origin coords: ● cell ○ abs
☐ Exclude region near spins: d-min = 2.0 Å
Symmetric sublattices: 1

2D Scan of Defined Plane
Origin: 0 0 2
X vector: 1 0 0
X min (Å): -8.714 X max (Å): 8.714
Y vector: 0 1 0
Y min (Å): -5.03 Y max (Å): 5.03
Origin/Vector Coords: ○ cell ● abs

3D Scan of Full Unit Cell
3D scan options: ☐ Use parallel cores ☐ Random sign of spin
Cell points=

Grid Array of Local Fields
☐ Cell average
z-plane 1
0.0

Field Distribution from Incommensurate SDW
q vector (cell) 0.0261 0.0261 0.0261
Mod vec1 (cell) 0 1 -1 Amp1 0.4
Mod vec2 (cell) 2 -1 -1 Amp2 0.4
Sample points 100 HF(G/muB) 0
○ Add moment ● Replace moment



kappa-(ET)2Cu[N(CN)2]Cl-100K (Pnma) - Mercury

Picking Mode: Pick Atoms
Style: Ball and Stick
Manage Styles... Publication
☐ Show Labels for
Default view: a

Press the left mouse button and move the mouse to rotate the structure