

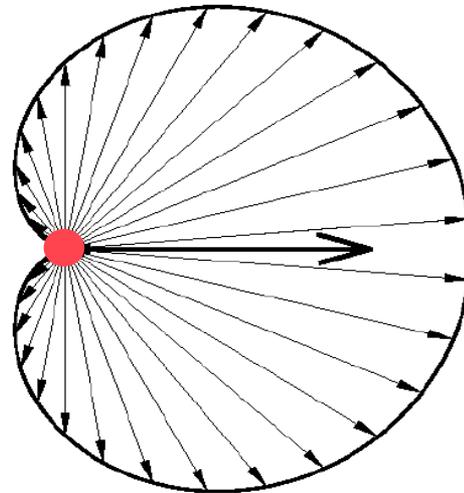
Computer Simulations for Interpreting μ SR Experiments

Leandro Liborio, Simone Sturniolo, Dominik Jochym,
Samuel Jackson

Theoretical and Computational Physics Group, SCD, STFC

Francis Pratt, Stephen Cottrell

ISIS Muon Group, STFC



1

Some fundamental approximations involved in our computer simulations. (Or a very brief introduction to Density Functional Theory).

2

How computer simulations can be used to assist in the interpretation of μ SR experiments in molecular systems.

3

The use of computer simulations for μ SR experiments in periodic crystalline systems. The problem of finding the muon stopping site .

4

Conclusions. Work in progress. Future plans.

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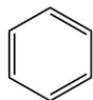
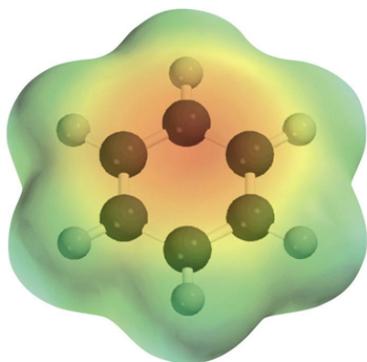
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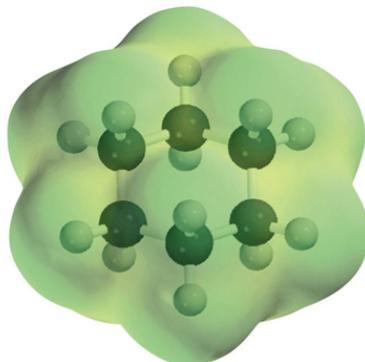
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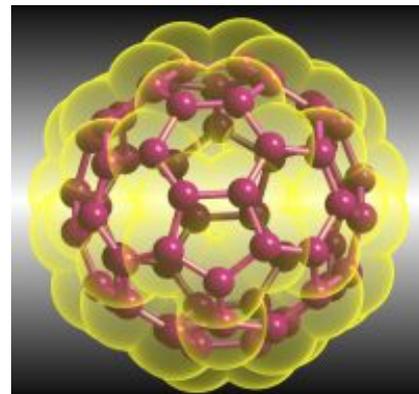
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benzene



cyclohexane



buckyball

Schrödinger equation contains most of a system's chemistry:

$$\hat{\mathcal{H}}[\Psi(r, \dots r_N; R_1, \dots R_M)] = E\Psi(r, \dots r_N; R_1, \dots R_M)$$

Born-Oppenheimer Approximation:

Assume that electronic relaxation is much faster than nuclei motion ($m_e \ll m_N$). Then can assume electrons move in the field of fixed nuclei.

$$\hat{\mathcal{H}}_{el}[\psi(r_1, \dots r_N)] = E_{el}\psi(r_1, \dots r_N)$$

WARNING: ($m_e \ll m_\mu$) NOT true for muons.

$$\hat{\mathcal{H}}[\Psi(r, \dots r_N; R_1, \dots R_M)] = E\Psi(r, \dots r_N; R_1, \dots R_M)$$



Born-Oppenheimer

$$\hat{\mathcal{H}}_{el}[\psi(r_1, \dots r_N)] = E_{el}\psi(r_1, \dots r_N)$$



DFT

- $n(r) = \langle \psi(r_1, \dots r_N) | \psi(r_1, \dots r_N) \rangle$ electronic density.
- $E_{el}[n]$ (PBE, B3LYP)
- $n(r) = \langle \varphi(r_1) \dots \varphi(r_N) | \varphi(r_1) \dots \varphi(r_N) \rangle$ system of fictional N-independent particles each represented by $\varphi(r_i)$.

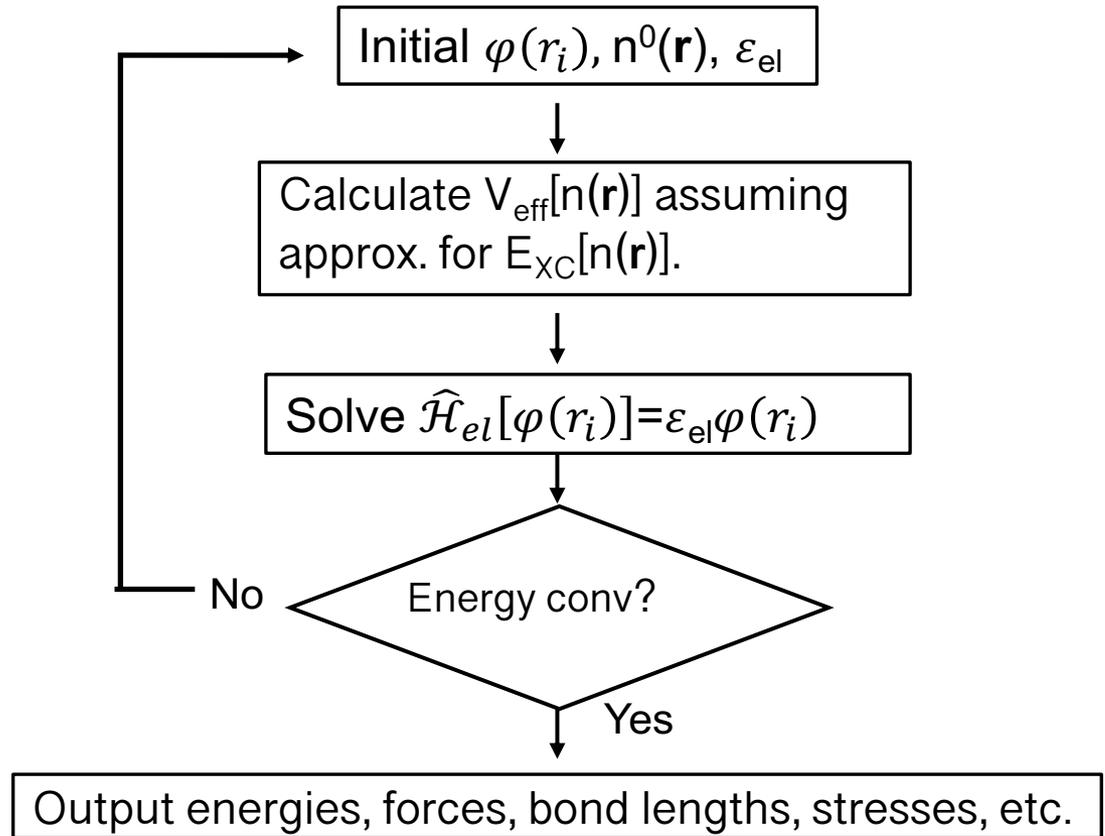
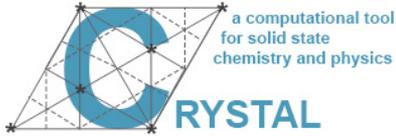
Black Box with Suitable Approximations



Can solve the Schrödinger equation and obtain an approximate energy and wave function for the system.



Gaussian



Obtain the relax structure and the total energy of the system

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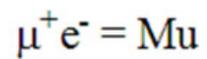
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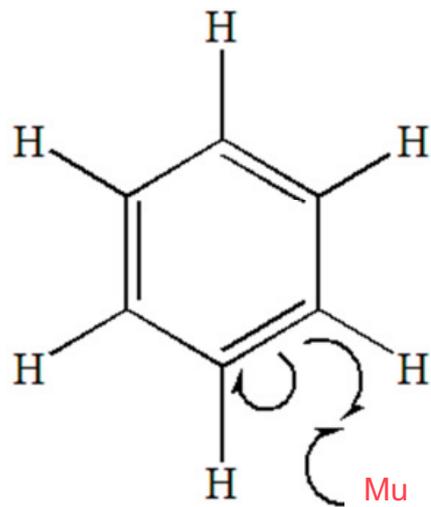
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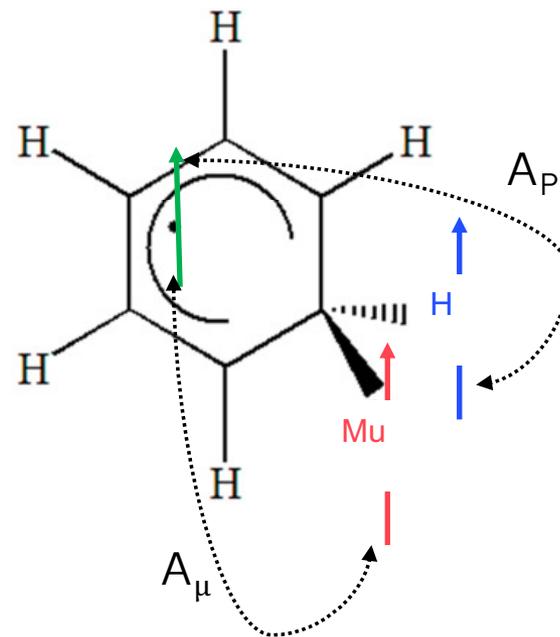
BENZENE



Delocalized unpaired electron



Muon adds across double bond



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

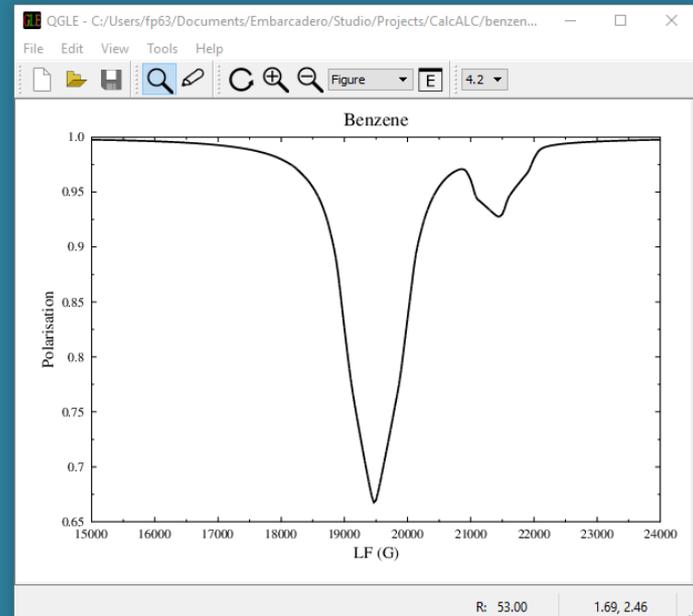
Spin state: doublet

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 Quantum/Calibration Factors
 A 1.230 D1 1.000 D2 1.000 Auto

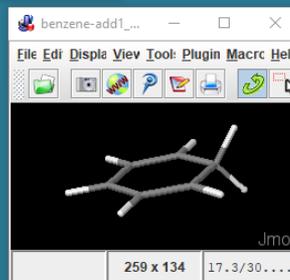
Nuclear Site Quantum/Calibration Factors
 A 0.96 D1 1.000 D2 1.000

Muon site: 13

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

Orientation averaging steps: 200

Solid State Liquid State

Table of Radicals Contributing to the ALC Spectrum

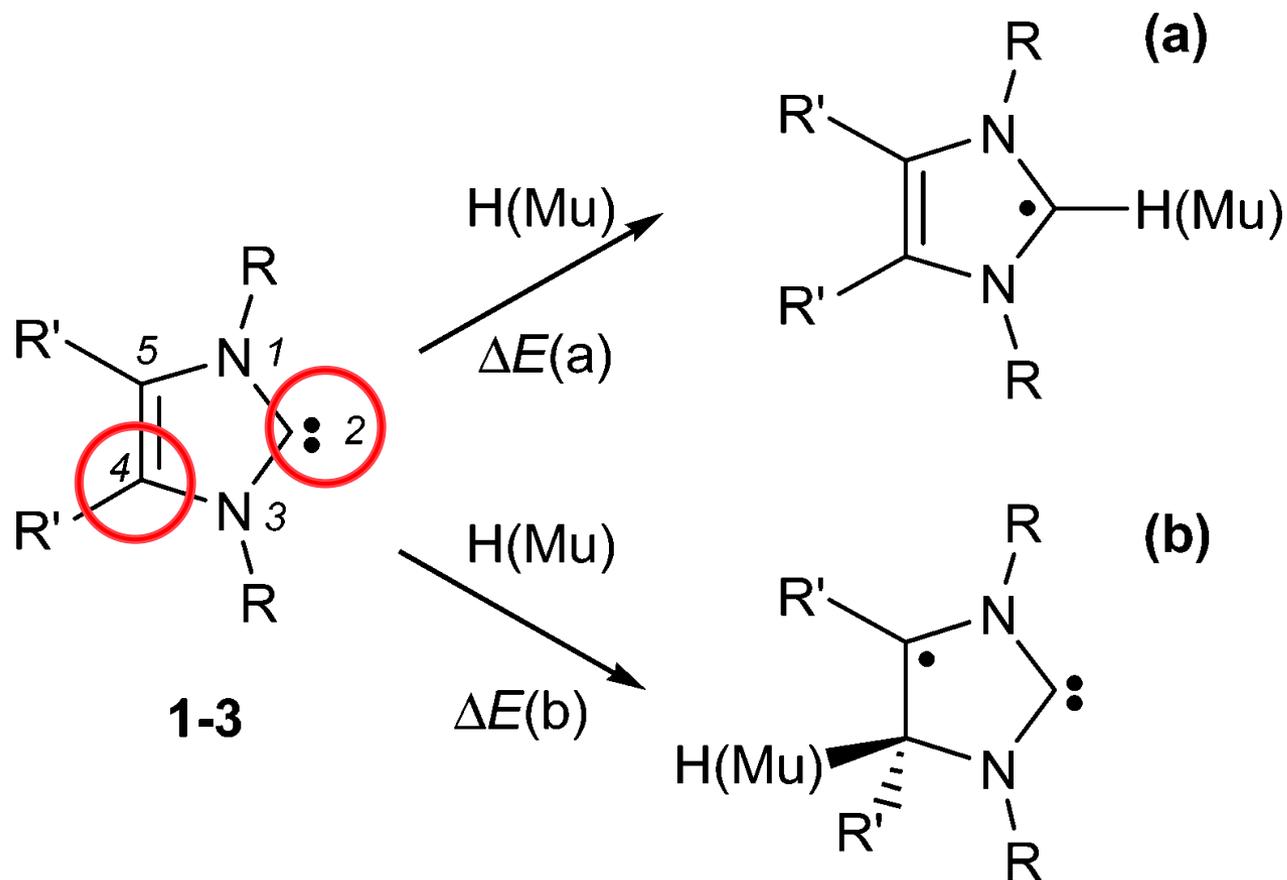
Radical #	Label	Mu/nucleu	Site numb	A-bare	A-factor	A	D1-bare	D1-factor	D1	D2-bare	D2-factor	D2	Weighting
1		Mu	13	431.46	1.230	530.7	12.80	1.000	12.8	12.10	1.000	12.1	1.000
		H	12	134.58	0.96	129.2	4.00	1.000	4.0	3.80	1.000	3.8	

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

Imidazole-type Carbene



Breit-Rabi diagram

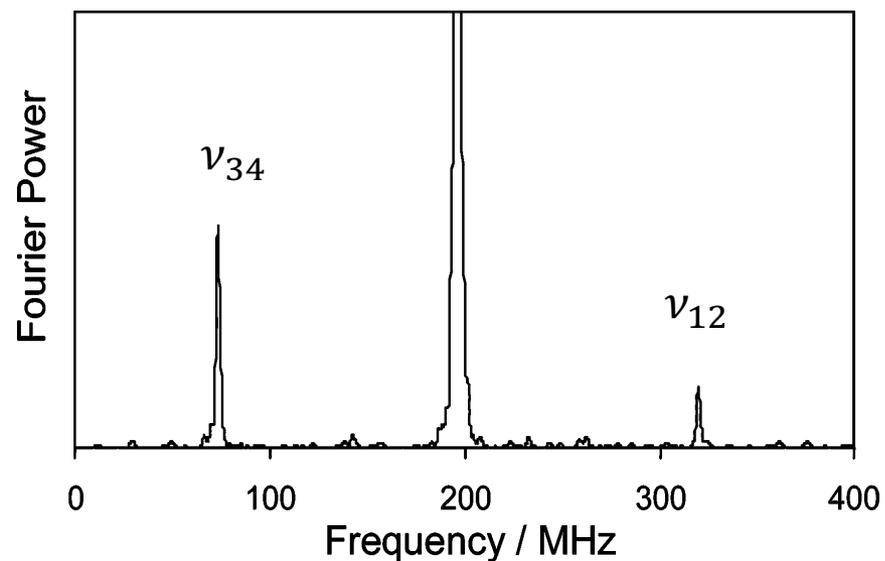
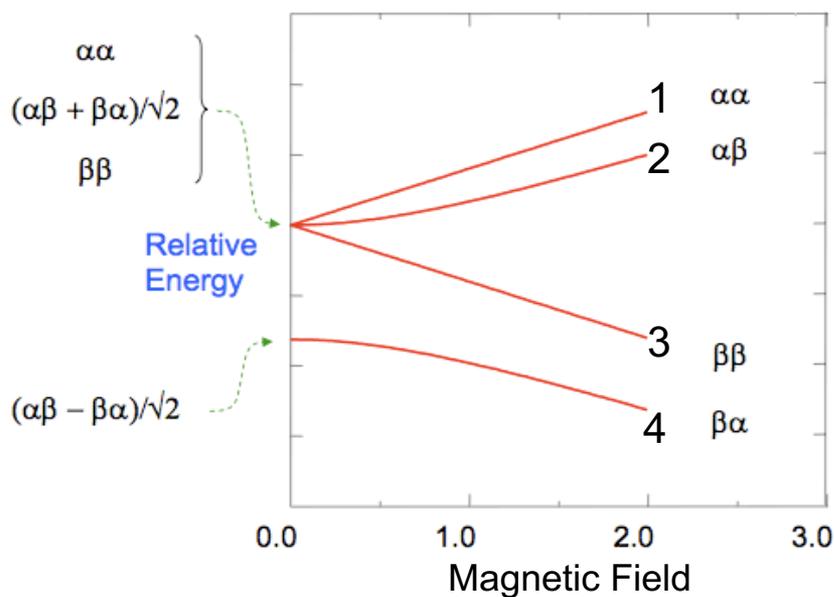
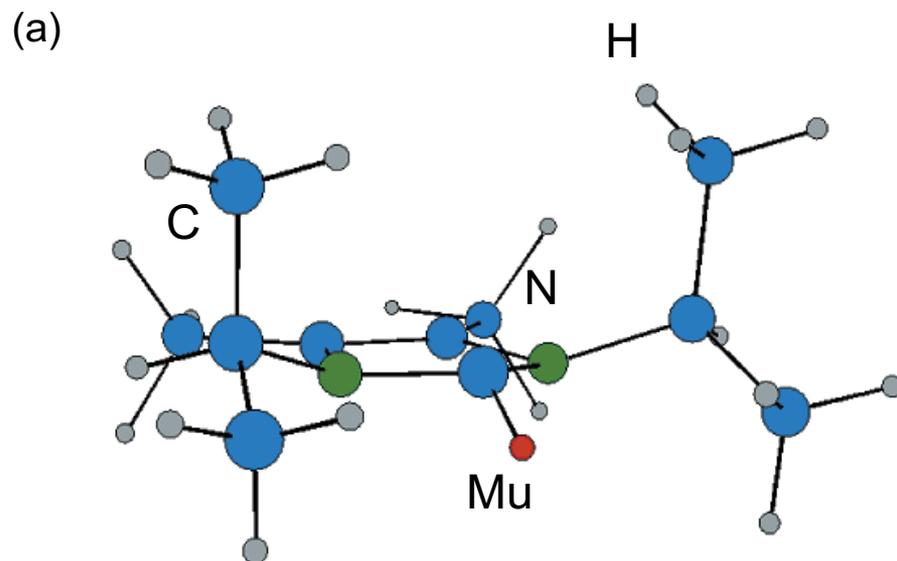
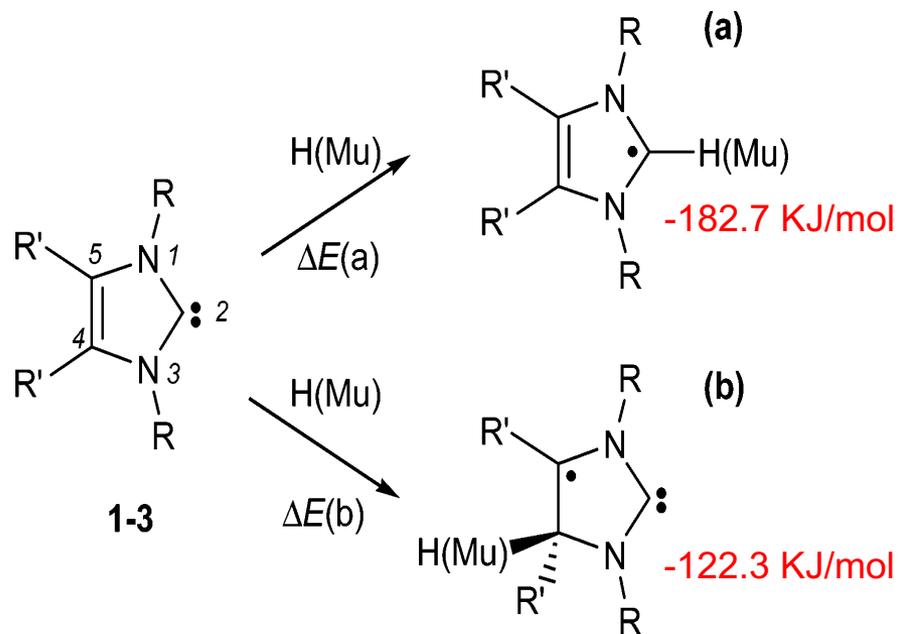


Figure 3. Transverse field μ SR spectrum at 14.4 kG from **1** in THF at 298 K. The pair of peaks at ca. 73 and 320 MHz is due to a muoniated radical.

- F- μ SR to calculate A_μ as

$$A_\mu = \nu_{12} - \nu_{34} = \mathbf{246.4 \text{ MHz}}$$



$A_\mu = 246.4 \text{ MHz}$ (adjusted to experiment)

- Used calculated reaction energies to place Mu in the molecule: (a) preferred site.

$$\Delta E(a) = E_{\text{radical.}} - (E_{\text{carbene.}} + E_H)$$

- Adjust the theoretical A_μ to agree with the experimental value.

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EXPERIMENTAL APPROACH

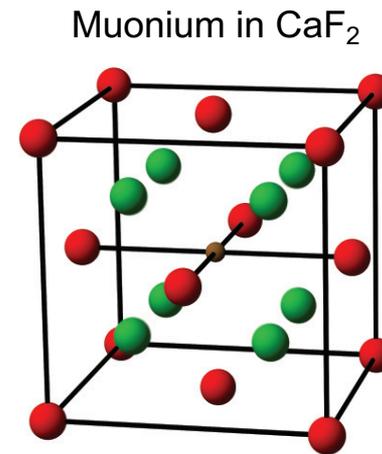
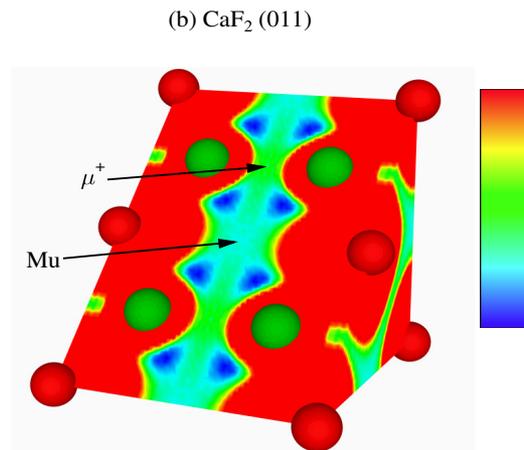
- Muonated Fe: follow the evolution of the muon frequency shift in a transverse field experiment as a function of the applied stress in a single Fe crystal¹

COMBINED THEORETICAL / EXPERIMENTAL APPROACH

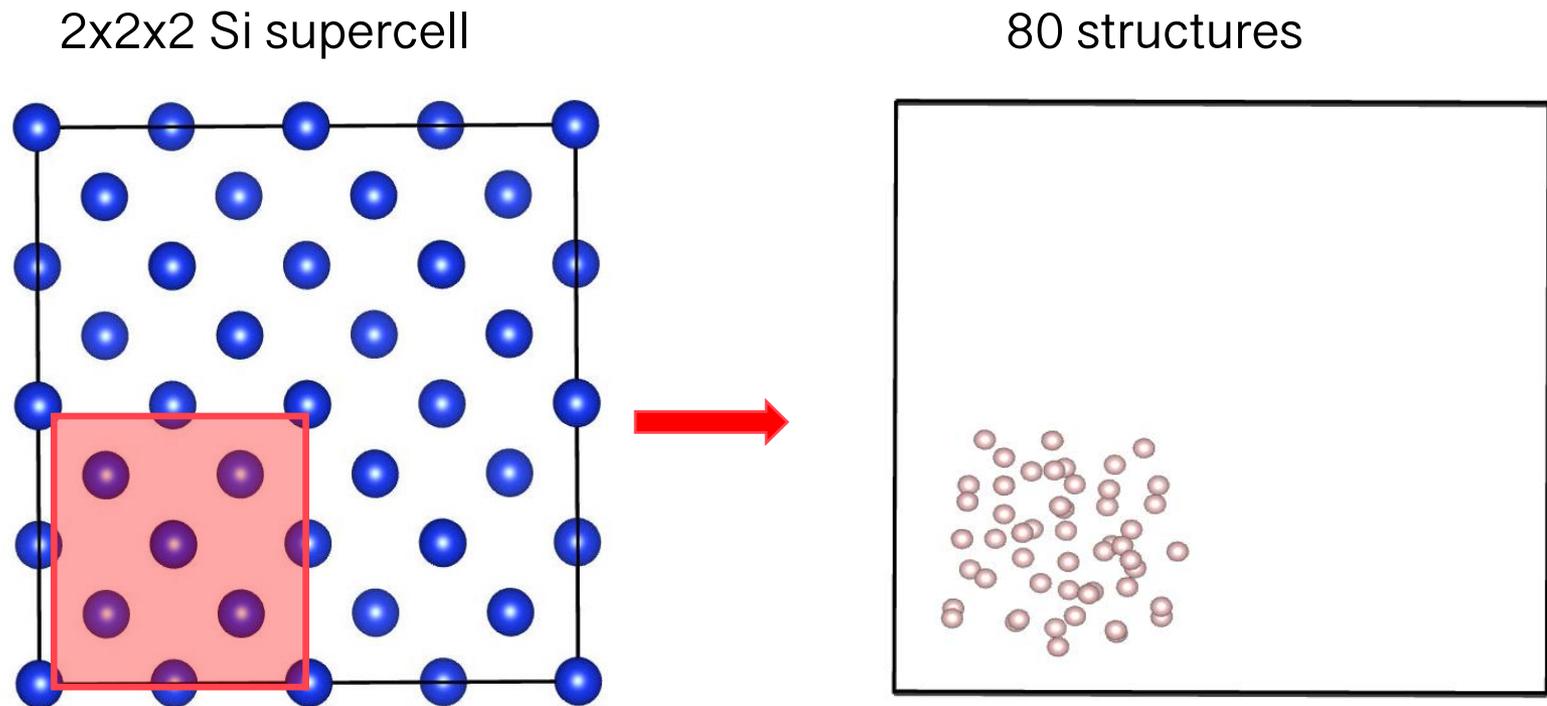
- Muonated Fe_3O_4 , ZnO and LiF: the theoretical calculations are used for testing different potential muon stopping sites

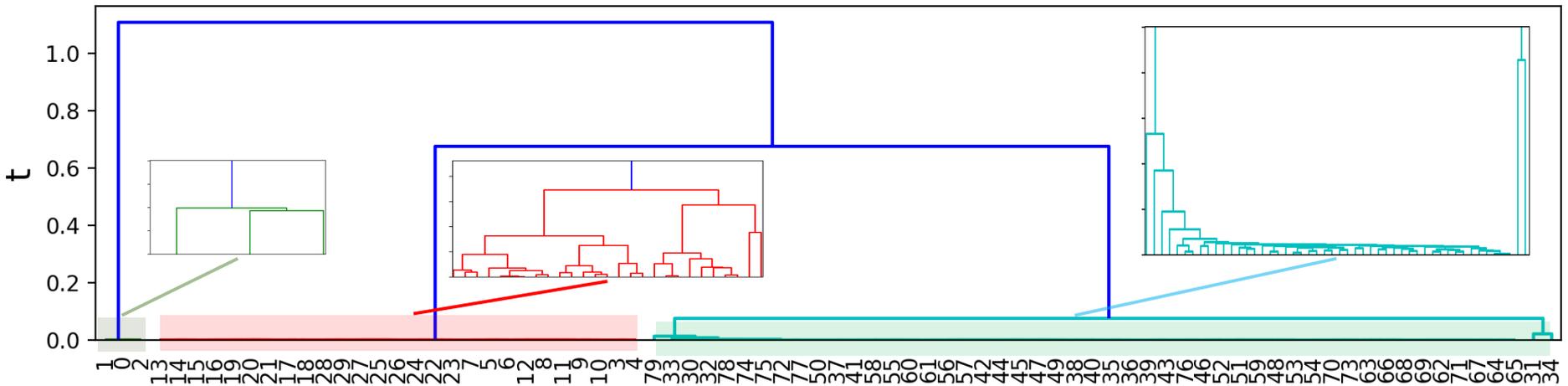
THEORETICAL APPROACH

- Approach that relies on the analysis of the electrostatic potential of the bulk material obtained from Density Functional Theory (DFT) simulations. This is known as the **Unperturbed Electrostatic Potential Method (UEP)**

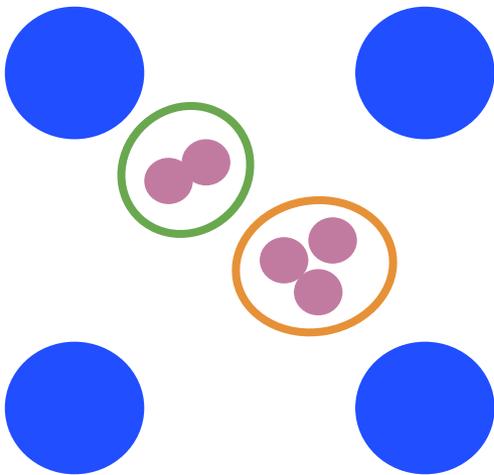


- 1) Build 2x2x2 Si supercell
- 2) Define region to randomly locate muonium pseudo-atoms
- 3) Generate muonated structures placing muonium in randomised positions within the chosen region
- 4) Relax filtered structures using calculated DFT forces

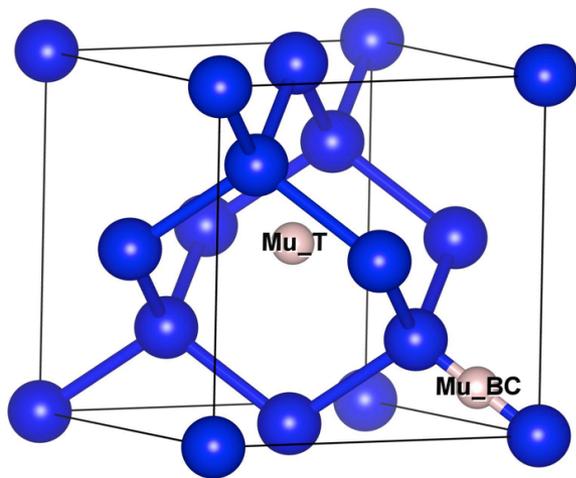
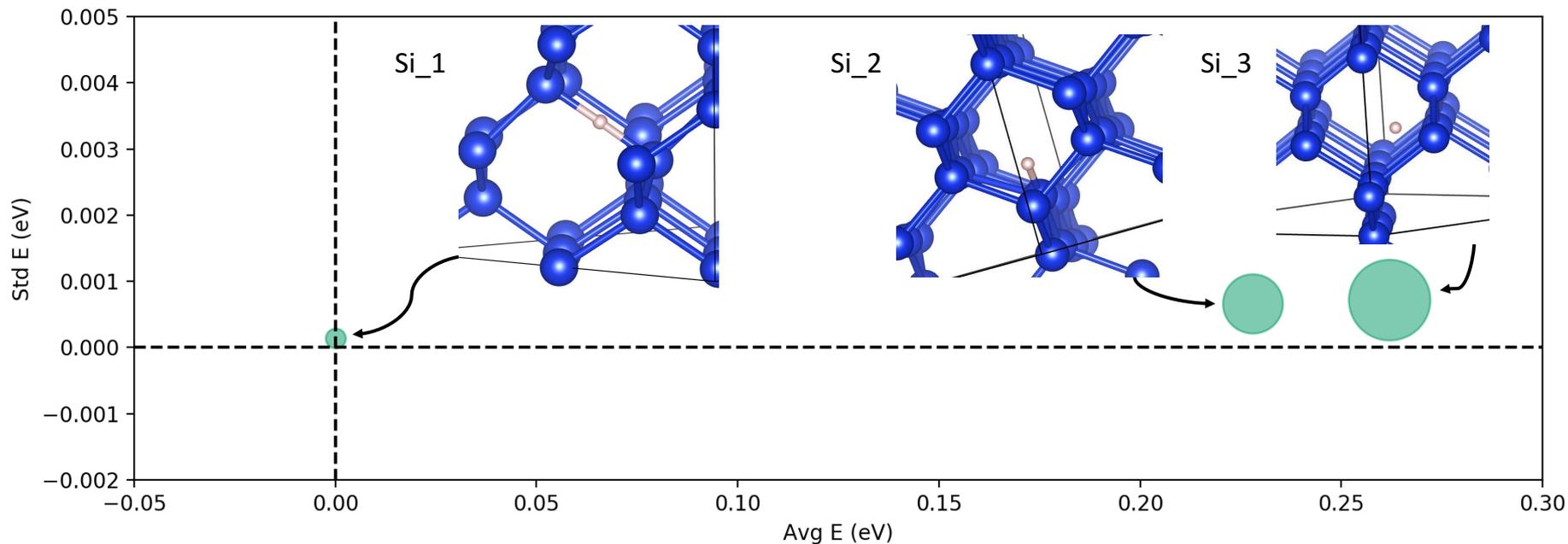




- Define n D vector: $(E_T, Q_1, Q_2, Q_3, \dots)$
- Look for “closeness” in n D space
- Hierarchical clustering
- 3 clusters identified



SOPRANO



- Identified 3 clusters
- Use k-means clustering
- Identified the Mu_T and M_{BC} in Silicon.



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CONCLUSIONS

1

DFT provides the basis for our computer simulations. Choose right code and XC functional for your system.

2

For molecules, standard DFT calculations can assist experiments, i.e.: help with ALC results.

3

For crystals, we can use simulations to predict the muon stopping site.

4

Working of using DFTB+, which may accelerate the calculations. Need to estimate the quantum effects.