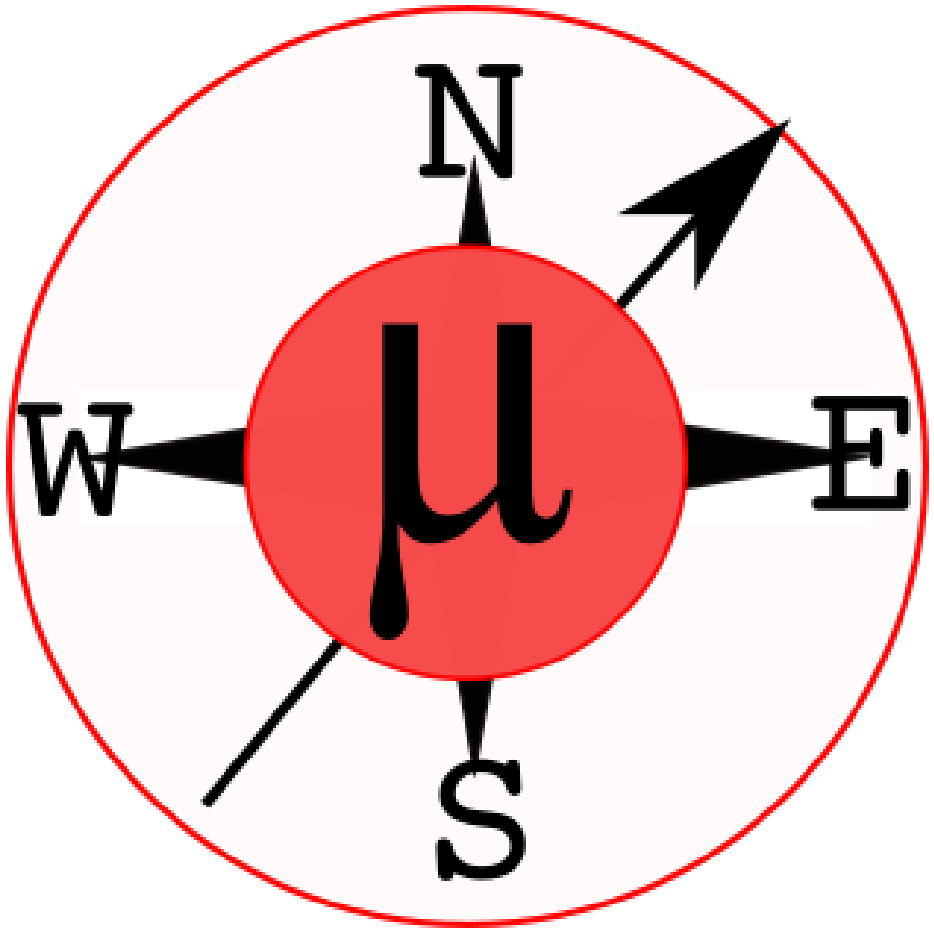
Durham University

MuFinder : A program to determine and analyse muon stopping sites



Ben Huddart

Durham University

https://gitlab.com/BenHuddart/mufinder

Outline of Talk

- The muon site problem and its solution, DFT+μ
- Introduction to MuFinder

Examples of muon site calculations

- Muon sites in 1T-TaS_2 – examining the possibility of delocalisation and/or diffusion
- Establishing the nature of muon stopping states in superconductors exhibiting spontaneous magnetic fields – is the muon a faithful probe?

The muon site problem

Two perceived defects of the μSR technique:

1. Our lack of knowledge of the muon stopping site;
2. the effect that a muon has on its environment

Address these using density functional theory (DFT) calculations

Density functional theory

- Condensed matter described by Schrodinger equation

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{ee}} + V_{\mathrm{en}}\right]\psi(r_1, \ldots, r_N) = E\psi(r_1, \ldots, r_N)$$

- DFT reformulates Schrödinger equation in terms of the electron density $n(\boldsymbol{r})$.
- Minimise $E[n(\boldsymbol{r})]$ to obtain ground state electron density
- Can be used to obtain structural, electronic and magnetic properties

DFT+μ

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **87**, 121108(R) (2013)

Quantum states of muons in fluorides

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(Received 23 December 2012; published 18 March 2013)

Muon-spin relaxation (μ^+SR) is a sensitive probe of magnetism, but its utility can be severely limited by the lack of knowledge of the muon implantation site and the extent to which the muon perturbs its host. We demonstrate systematically that these problems can be addressed accurately using electronic-structure calculations. We show that diamagnetic muons introduce significant short-ranged distortions in ionic insulators that would lead to systematic errors on magnetic moments determined by μ^+SR, and quantify these. The F-μ-F complex formed by muons in many fluorides can be understood as an exotic molecule-in-a-crystal defect with a zero-point energy larger than that of any naturally occurring triatomic molecule.

DOI: 10.1103/PhysRevB.87.121108 PACS number(s): 76.75.+i, 71.15.Mb, 75.25.−j

PHYSICAL REVIEW B **87**, 115148 (2013)

Ab initio strategy for muon site assignment in wide band gap fluorides

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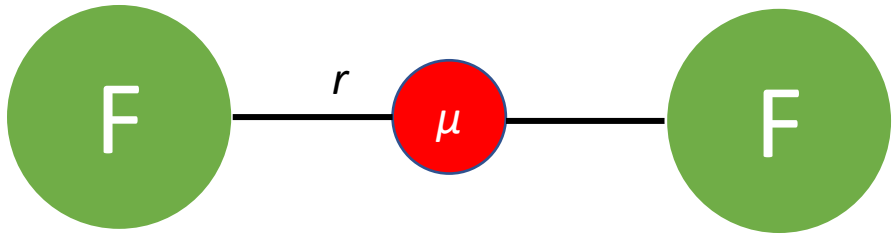
(Received 16 January 2013; published 29 March 2013)

We report on an *ab initio* strategy based on density functional theory to identify the muon sites. Two issues must be carefully addressed: muon delocalization about candidate interstitial sites and local structural relaxation of the atomic positions due to μ^+-sample interaction. Here, we verify our strategy's validity focusing on two wide band gap materials, LiF and YF_3, where both μ^+ delocalization and crystal lattice relaxation play an important role in determining the μ^+ stopping site positions.

DOI: 10.1103/PhysRevB.87.115148 PACS number(s): 76.75.+i, 71.15.Mb, 76.60.Jx



DFT+μ

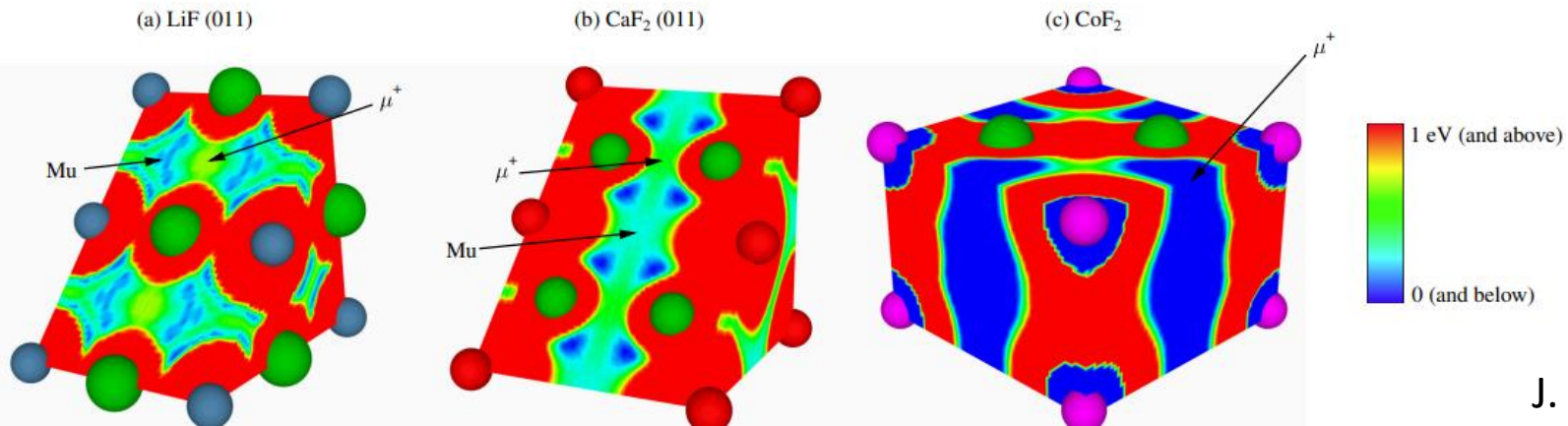
Two common approaches:

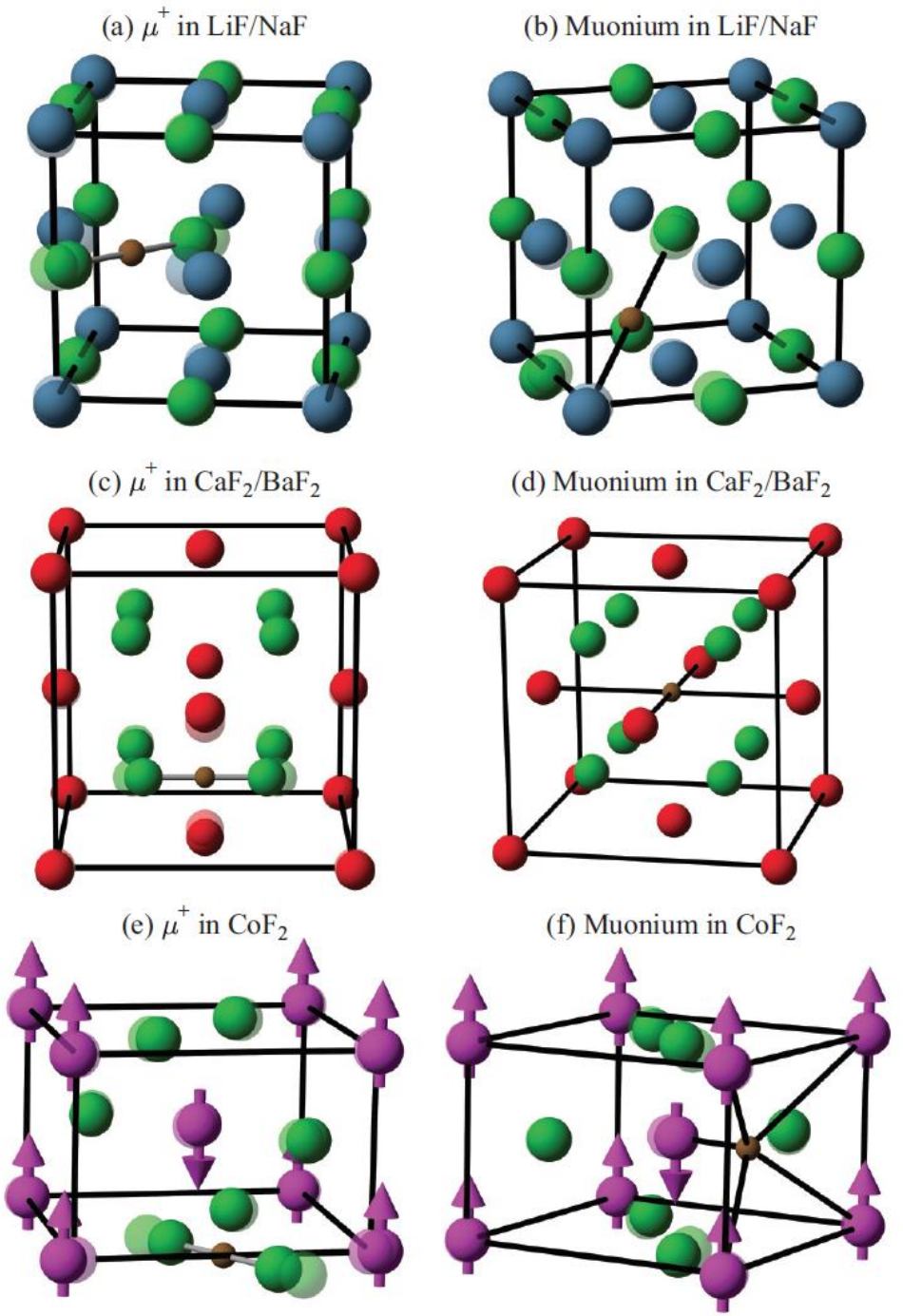
1. **Unperturbed electrostatic potential (UEP) method:** As a positively charged defect, μ^+ is likely to stop at the minima of the electrostatic potential of the crystal.

2. **Structural relaxation:** A muon (modelled by a proton) is added to the structure and the structure is relaxed using forces calculated from DFT.

DFT+μ

- Electrostatic potential not always an accurate predictor of muon stopping sites
- Structural relaxation approach allows muon-induced distortions to be assessed



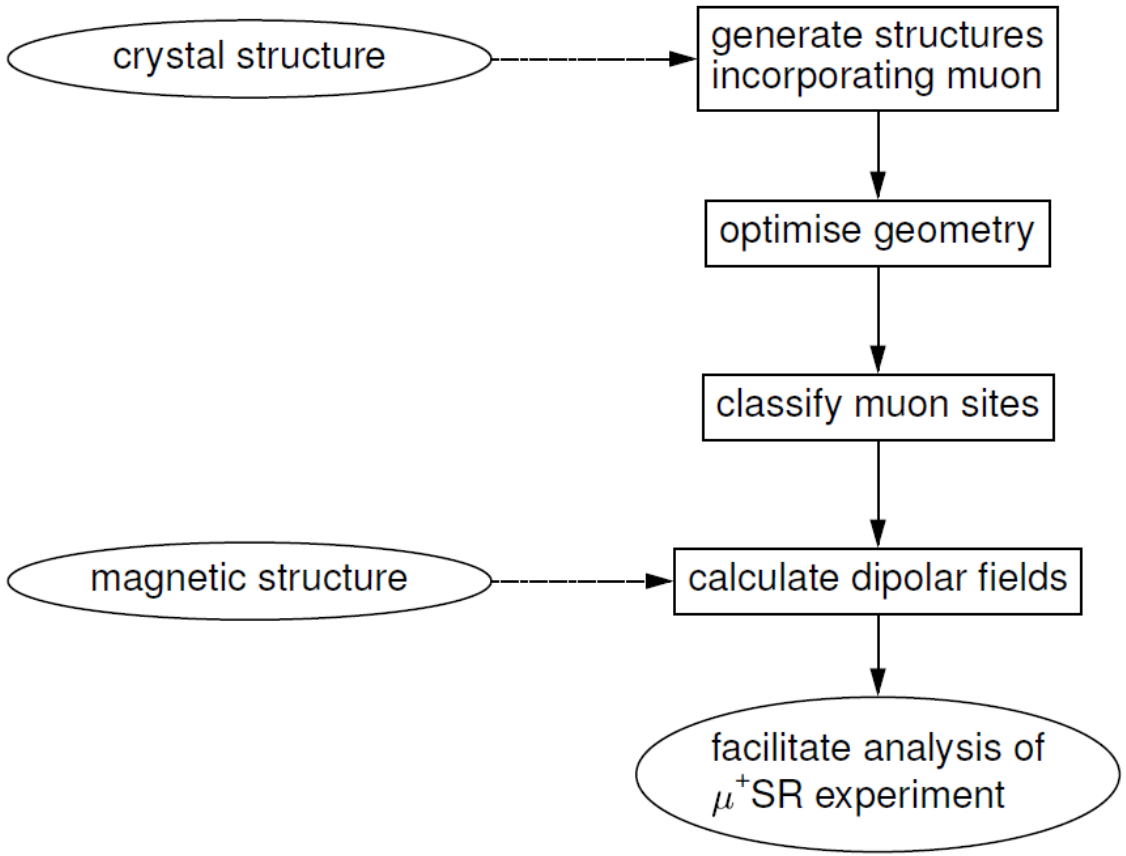


J. S. Möller *et al.* Phys. Rev. B **87,** 121108(R) (2013)

MuFinder

- MuFinder aims to make these methods more accessible by allowing these calculations to be run through a simple graphical user interface (GUI)

- It has been designed to automate the workflow required to calculate muon sites using the structural relaxation method



Design principles

Python GUI application that makes use of the following libraries:

- Atomic Simulation Environment (ASE): For manipulation and visualisation of structures
- Soprano: For handling collections of structures
- MuESR (Magnetic structure and mUon Embedding Site Refinement): to calculate the local magnetic field at the muon stopping site

Initial muon position generation

- In general, there will be more than one (meta)stable muon stopping site
- Hence, we need to sample multiple initial muon positions to identify all the distinct minima
- Each initial muon position requires a geometry optimisation calculation
- Want to minimise number of initial positions while ensuring sufficient sampling of the distinct positions within the unit cell

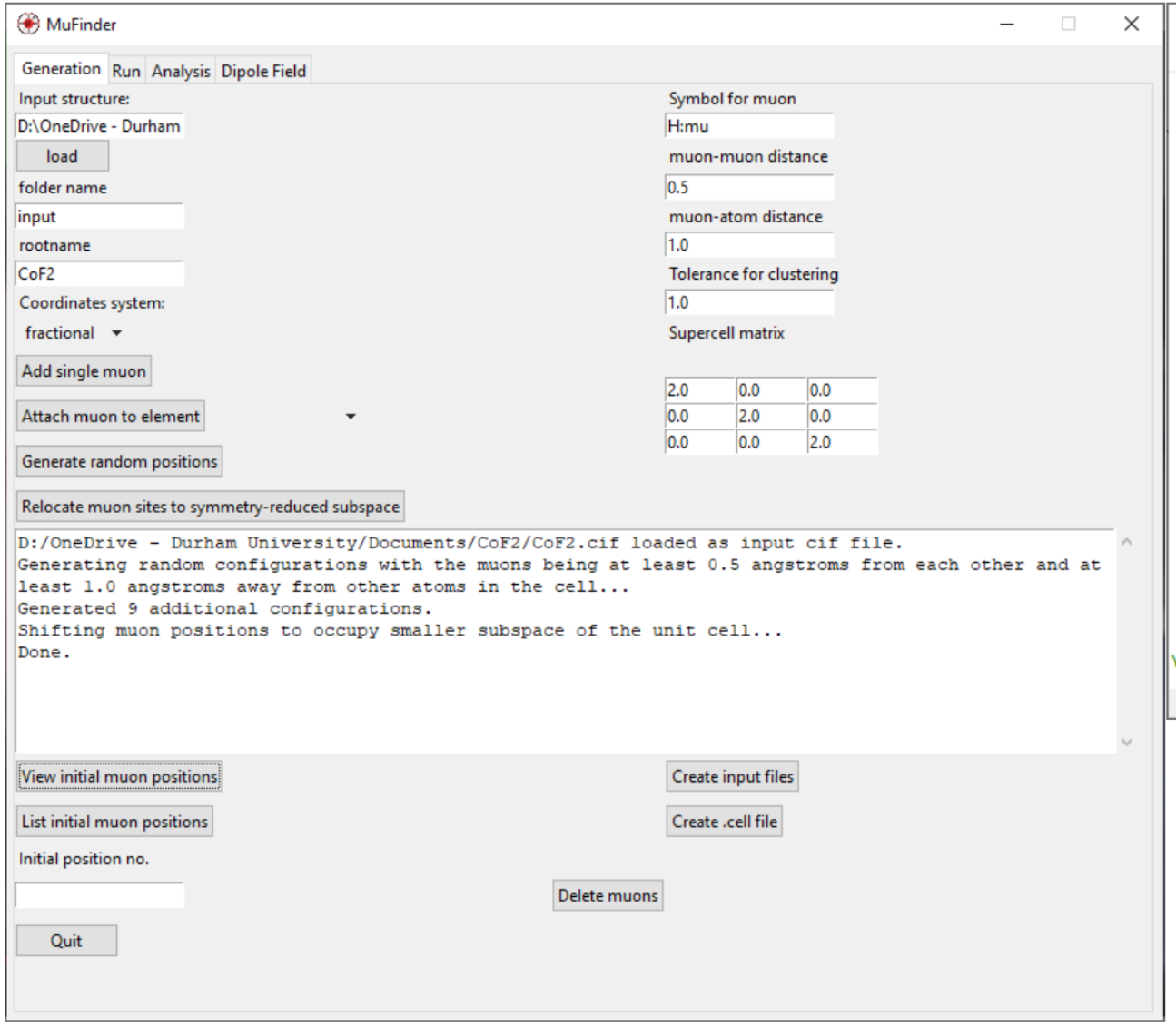
Initial muon position generation

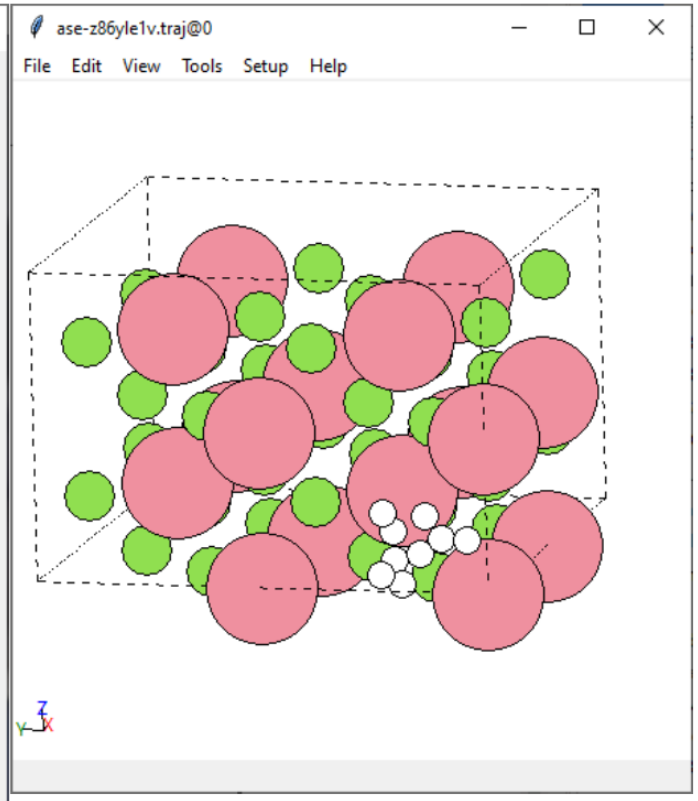
1. Generate random positions in the conventional unit cell.

2. Accept each position if it and its symmetry equivalent positions within the unit cell are all:
   (i) at least r_{muon} away from the other initial muons positions and
   (ii) at least r_{atom} away from all of the atoms in the cell.

3. Repeat until 30 new positions are rejected.

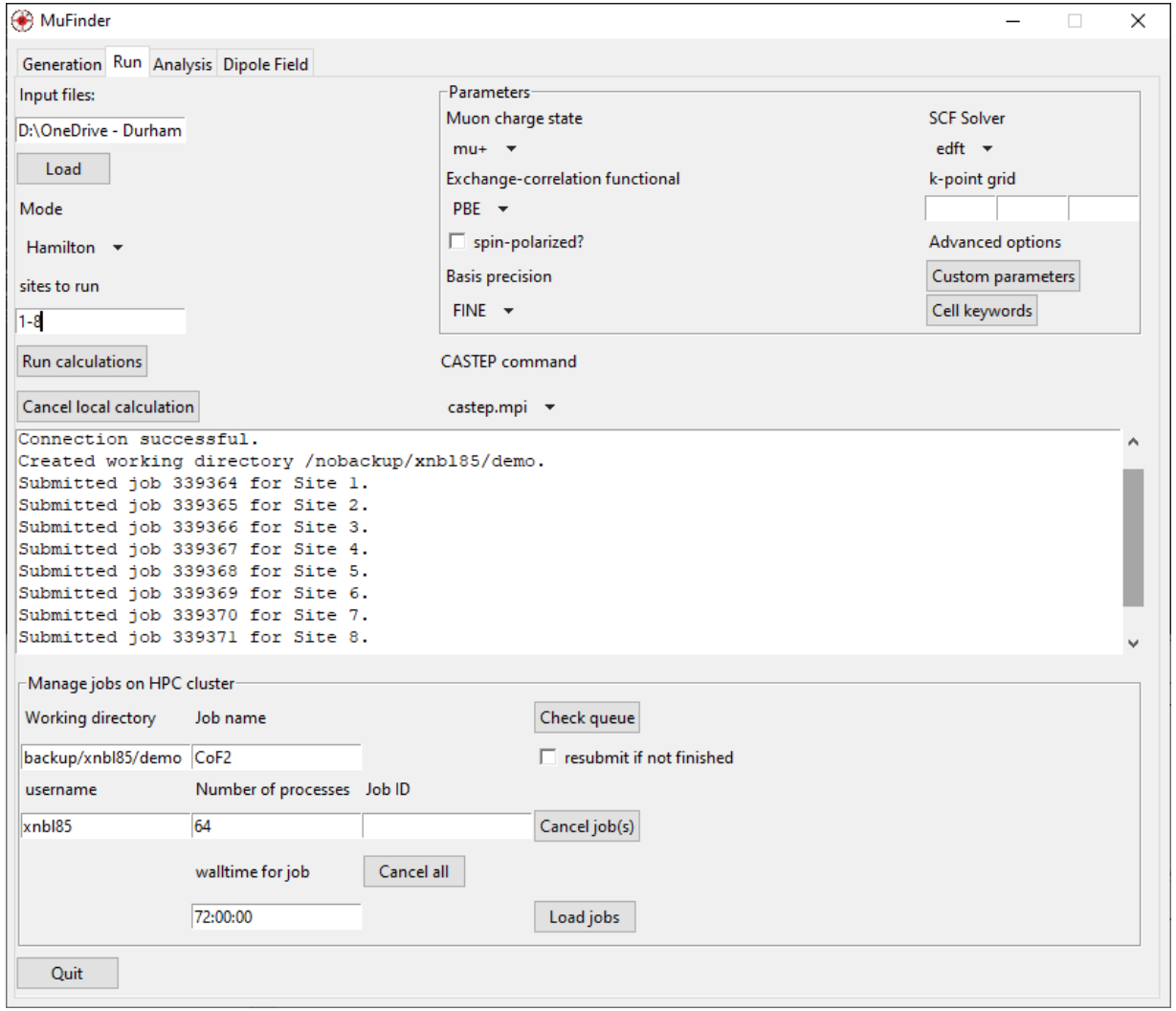
Initial muon position generation





Running the calculations

- Jobs can be run using a local CASTEP installation or on a remote cluster
- For jobs run on a cluster, MuFinder can be used to monitor the status of jobs and will collect the output files once jobs have finished



Clustering algorithm

1. Construct the distance matrix **D** where D_{ij} are the minimum distances between muon sites *i* and *j* along with symmetry equivalent positions.

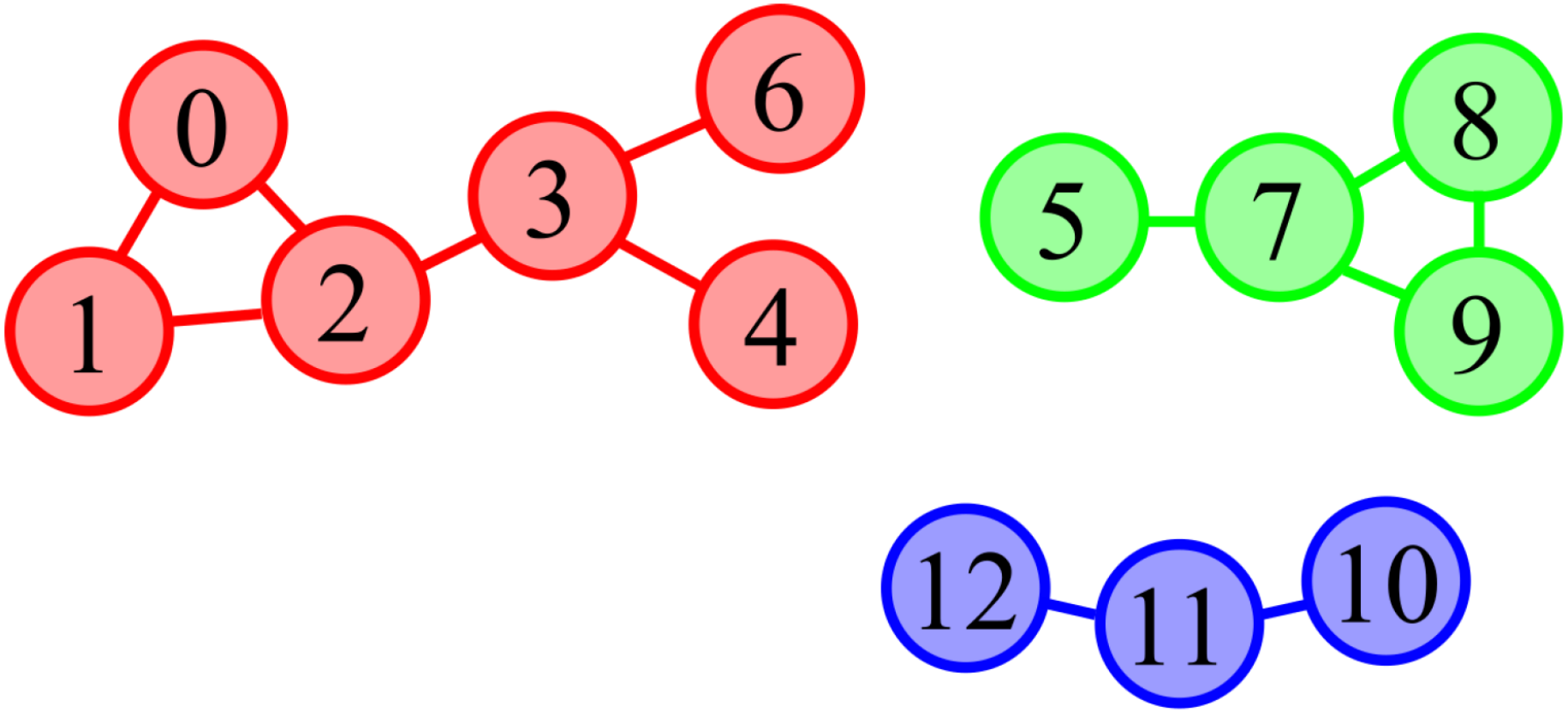
2. Construct the adjacency matrix **A** where

$$A_{ij} = \begin{cases} 1, & i \neq j, D_{ij} < d_{\max} \\ 0, & \text{otherwise} \end{cases}$$

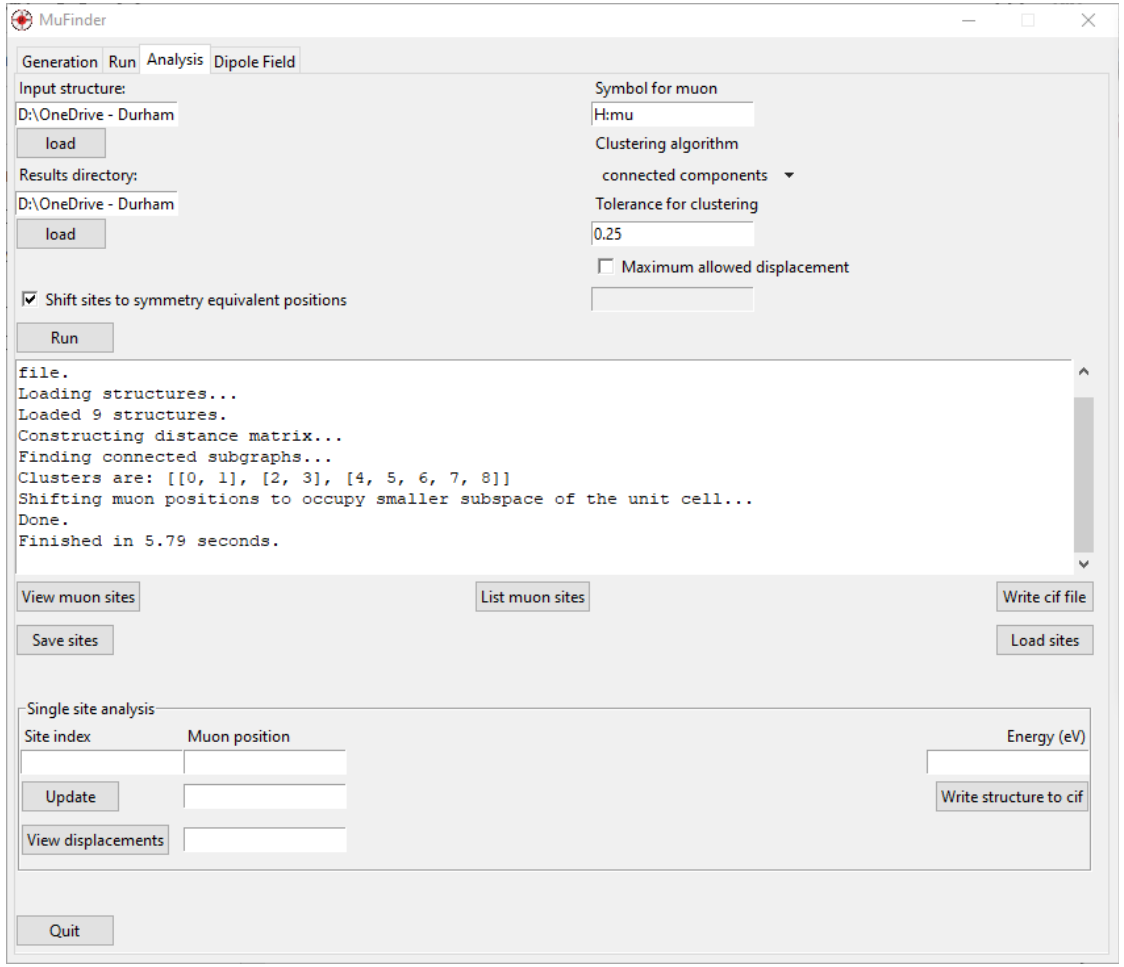
with $d_{\max}$ being the maximum distance between muon sites for them to be considered *connected*.

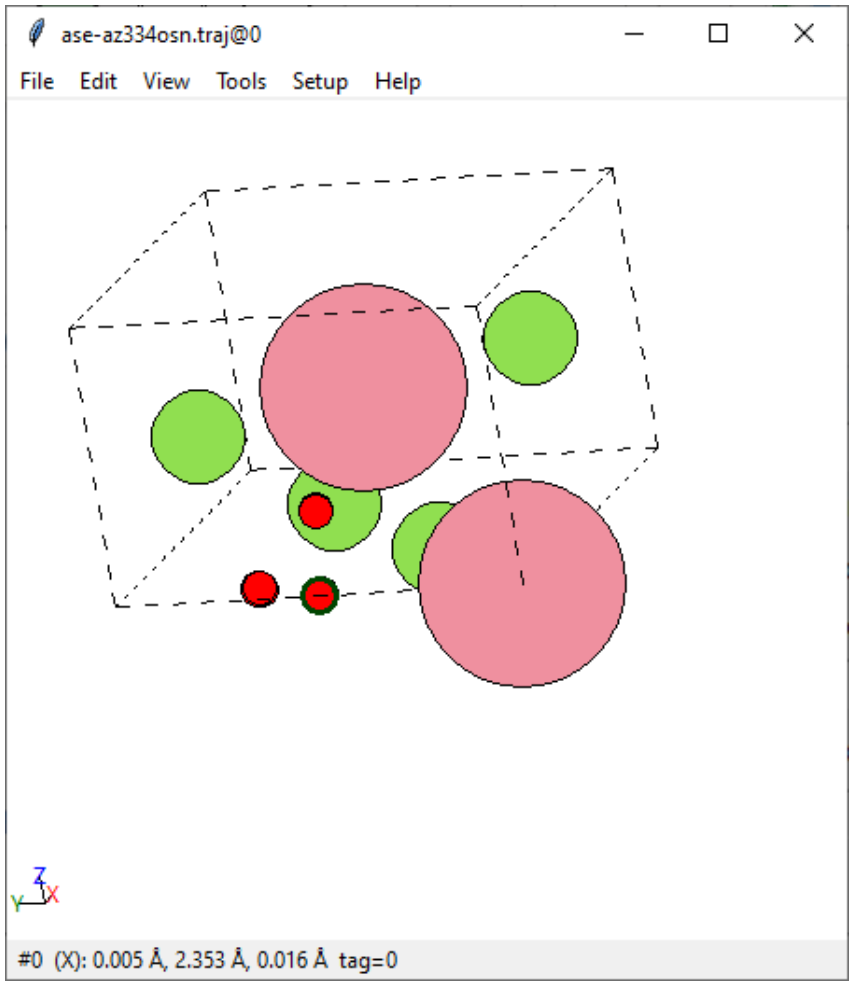
3. Find the connected components of **A**. These are the clusters of muon sites.

Connected components



Analysis

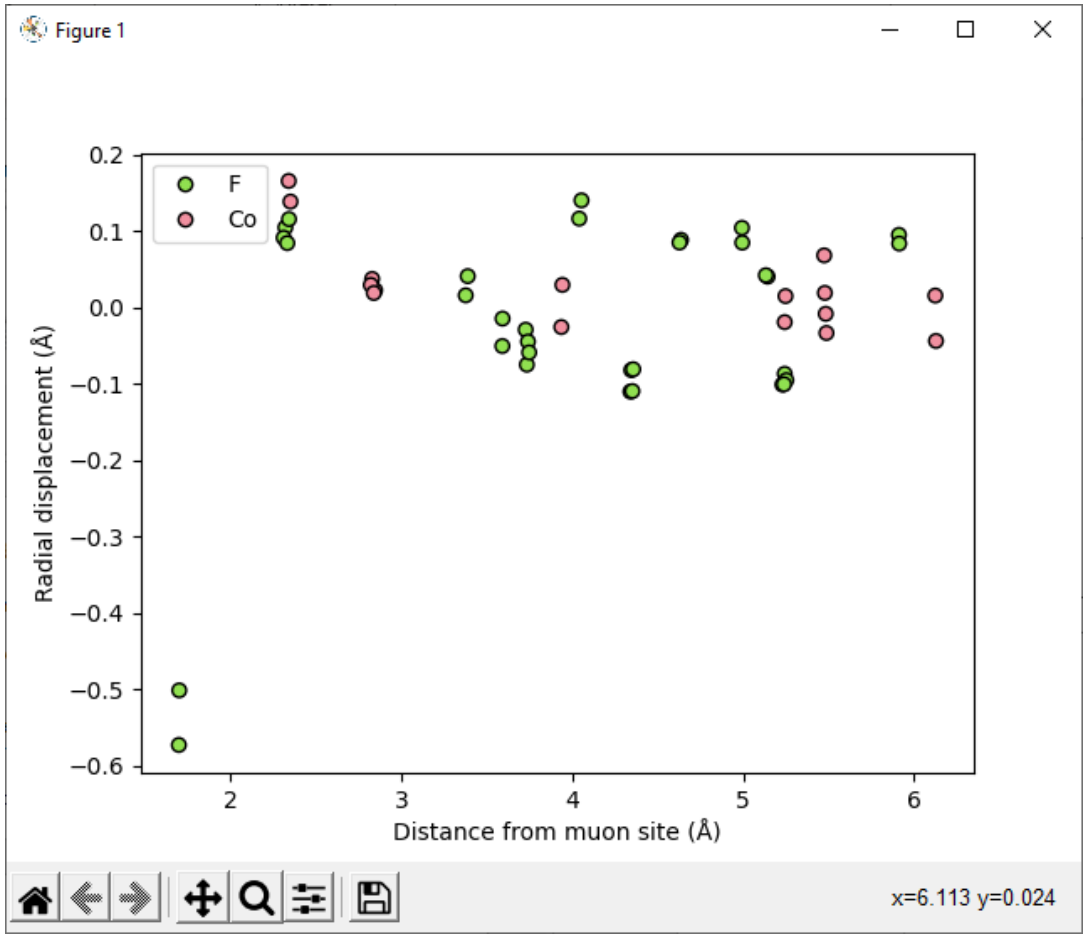

MuFinder
Generation
Run
Analysis
Dipole Field
Input structure:
D:\OneDrive - Durham
load
Results directory:
D:\OneDrive - Durham
load
Symbol for muon
H:mu
Clustering algorithm
connected components
Tolerance for clustering
0.25
Maximum allowed displacement
Shift sites to symmetry equivalent positions
Run
file.
Loading structures...
Loaded 9 structures.
Constructing distance matrix...
Finding connected subgraphs...
Clusters are: [[0, 1], [2, 3], [4, 5, 6, 7, 8]]
Shifting muon positions to occupy smaller subspace of the unit cell...
Done.
Finished in 5.79 seconds.
View muon sites
List muon sites
Write cif file
Save sites
Load sites
Single site analysis
Site index
Muon position
Energy (eV)
Update
Write structure to cif
View displacements
Quit


ase-az334osn.traj@0
File
Edit
View
Tools
Setup
Help
#0 (X): 0.005 Å, 2.353 Å, 0.016 Å tag=0

Analysis

- The structural relaxation method provides the full relaxed structure of the system + implanted muon (not just the muon site)

- This allows us to assess the significance of any muon-induced distortions



Dipole fields - theory

- Dipole fields calculated using MuESR

$$\boldsymbol{B}_{\mathrm{dip}} = \frac{\mu_0}{4\pi} \sum_{i=1}^{N} \left(-\frac{\boldsymbol{m}_i}{r_i^3} + \frac{(\boldsymbol{m}_i \cdot \boldsymbol{r}_i)\boldsymbol{r}_i}{r_i^5} \right).$$

- Magnetic structure described using propagation vector formalism

$$\boldsymbol{m}_{n\nu} = \sum_{\mathbf{k}} S_{\nu\mathbf{k}} e^{-2\pi i \mathbf{k}\cdot\mathbf{R}_n},$$

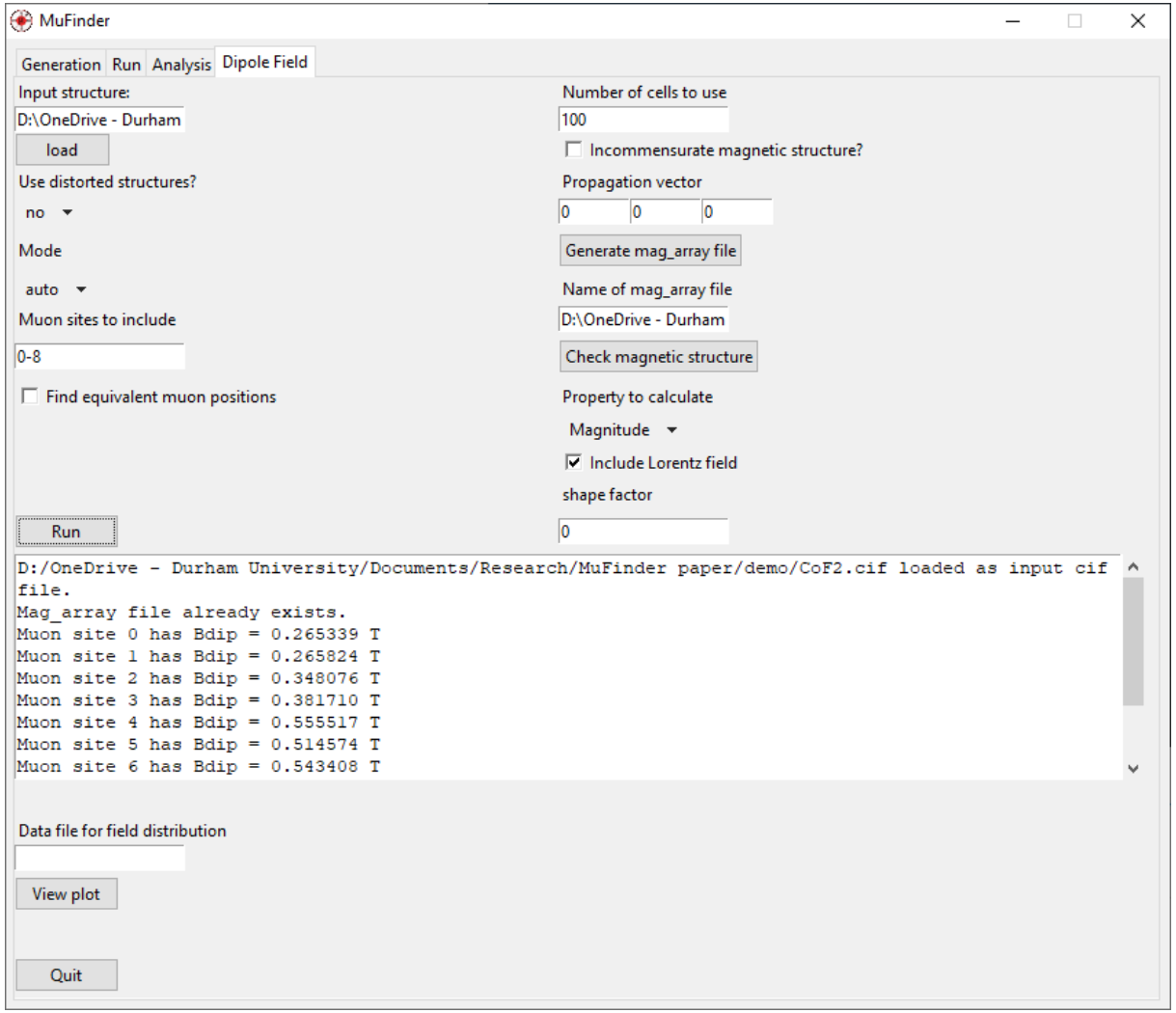
where ν runs over the atoms in the unit cell and *n* identifies the *n*th unit cell with atomic positions

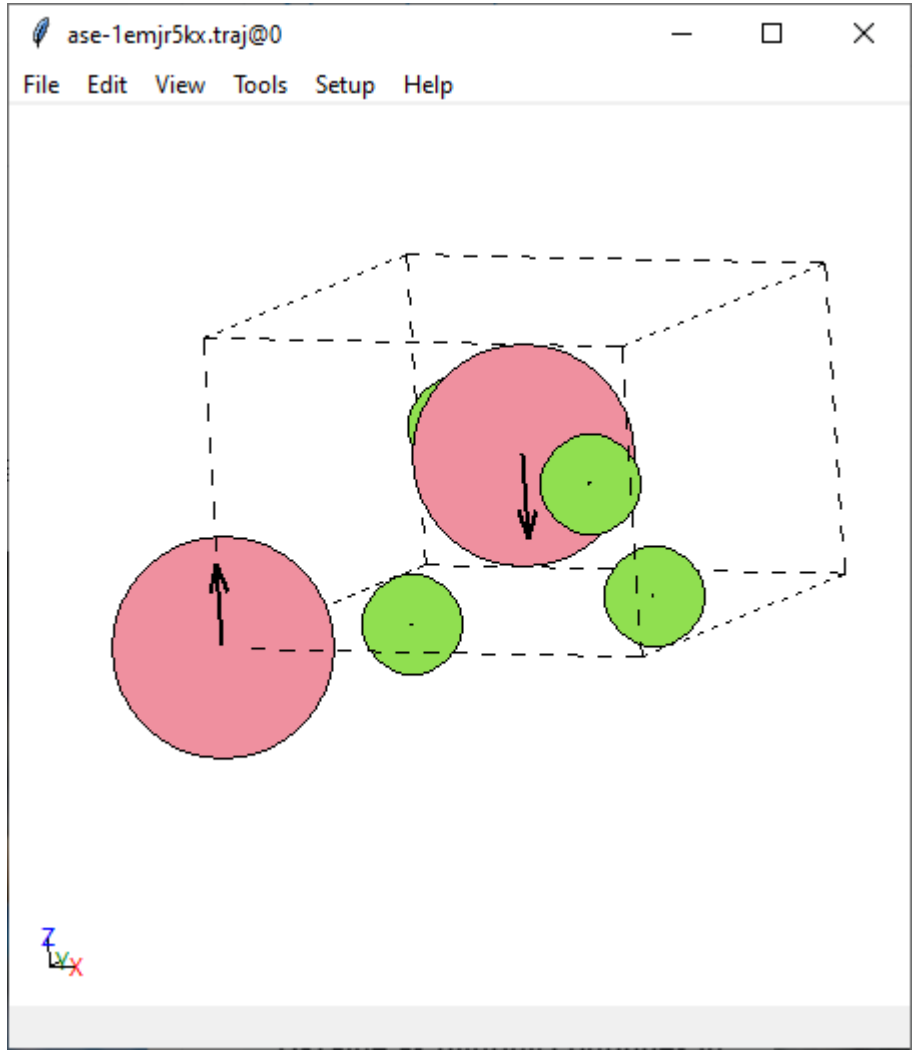
$$\mathbf{R}_{n\nu} = \mathbf{R}_n + \boldsymbol{r}_\nu.$$

- User defines propagation vector for the magnetic structure and the complex coefficients for each atom in the unit cell.

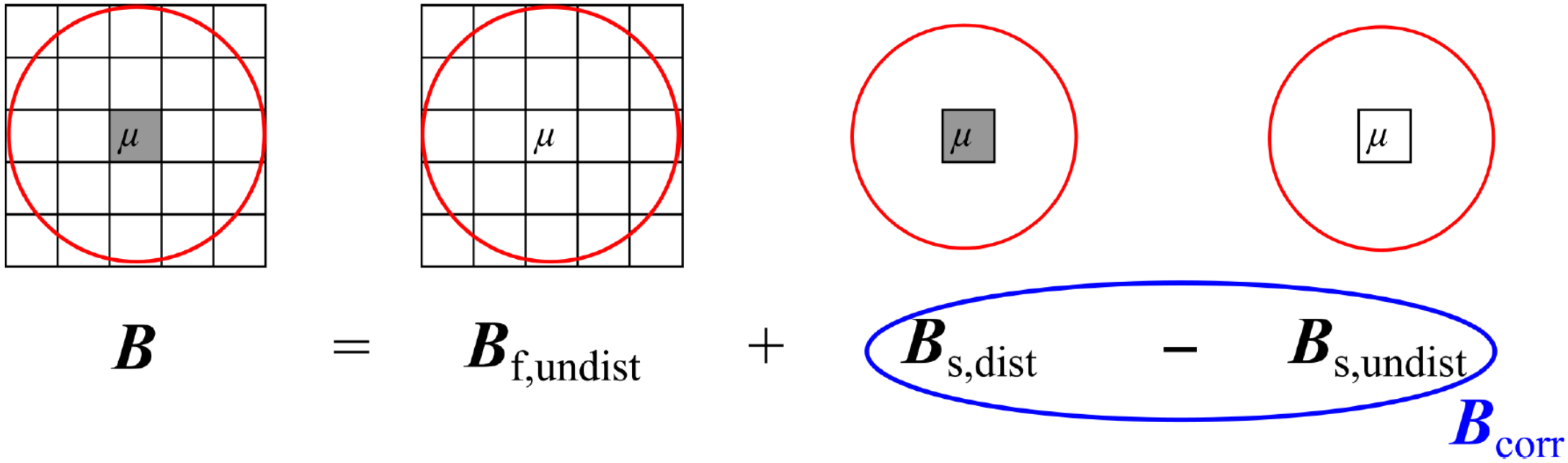
```
elem,a,b,c,mxr,mxi,myr,myi,mzr,mzi
Co,0.0,0.0,0.0,0,0,0,0,2.64,0
Co,0.5,0.5,0.5,0,0,0,0,-2.64,0
F,0.195981,0.804019,0.5,0,0,0,0,0,0
F,0.804019,0.195981,0.5,0,0,0,0,0,0
F,0.695981,0.695981,0.0,0,0,0,0,0,0
F,0.304019,0.304019,0.0,0,0,0,0,0,0
```

Dipole fields - calculation





Simulating distorted structures



Dipole fields - summary

Experiment[1]	0.228 T	
	Undistorted	Distorted
Möller et al.[2]	0.265 T	0.208 T
MuFinder	0.265 T	0.207 T

1. R. De Renzi *et al.* Phys Rev. B **30**, 186 (1984)
2. J. S. Möller *et al.* Phys. Rev. B **87,** 121108(R) (2013)

MuFinder in practice – examples from research

Example 1 – Muon hyperfine coupling and delocalisation in 1T-TaS_2

npj | Quantum Materials

www.nature.com/npjquantmats

ARTICLE OPEN

Check for updates

Quantum phases and spin liquid properties of 1T-TaS_2

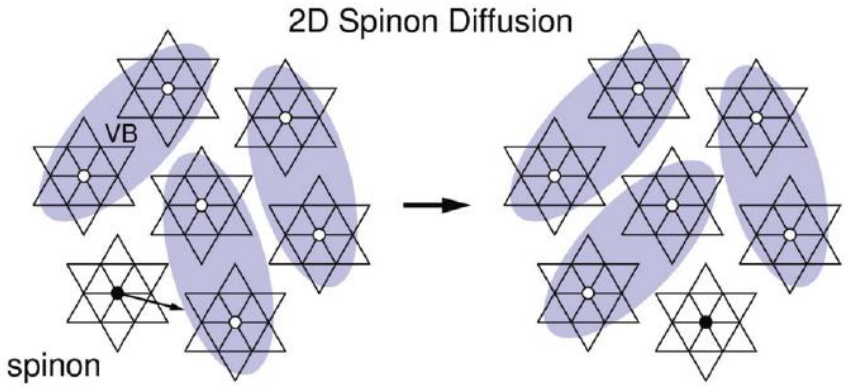
Samuel Mañas-Valero[1], Benjamin M. Huddart[2], Tom Lancaster[2], Eugenio Coronado[1] and Francis L. Pratt[3]✉

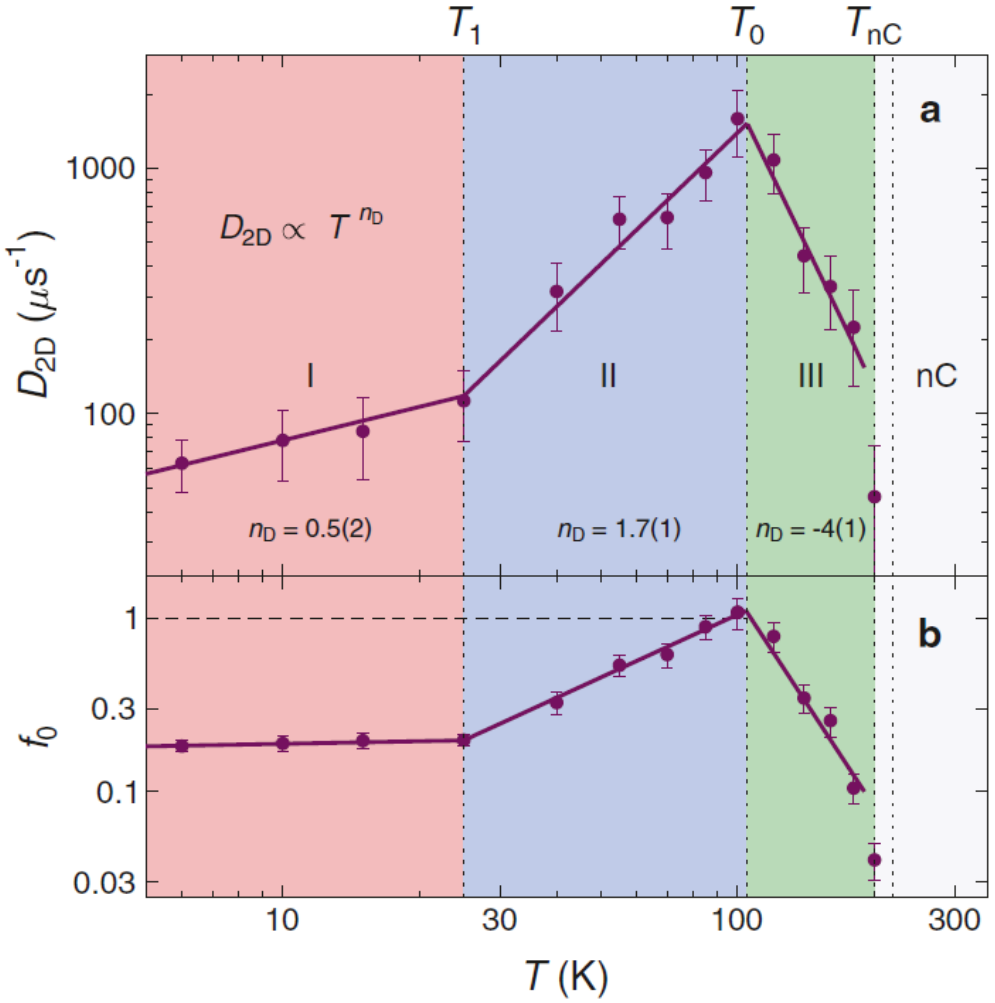
Quantum materials exhibiting magnetic frustration are connected to diverse phenomena, including high T_c superconductivity, topological order, and quantum spin liquids (QSLs). A QSL is a quantum phase (QP) related to a quantum-entangled fluid-like state of matter. Previous experiments on QSL candidate materials are usually interpreted in terms of a single QP, although theories indicate that many distinct QPs are closely competing in typical frustrated spin models. Here we report on combined temperature-dependent muon spin relaxation and specific heat measurements for the triangular-lattice QSL candidate material 1T-TaS_2 that provide evidence for competing QPs. The measured properties are assigned to arrays of individual QSL layers within the layered charge density wave structure of 1T-TaS_2 and their characteristic parameters can be interpreted as those of distinct Z_2 QSL phases. The present results reveal that a QSL description can extend beyond the lowest temperatures, offering an additional perspective in the search for such materials.

npj Quantum Materials (2021)6:69 ; https://doi.org/10.1038/s41535-021-00367-w

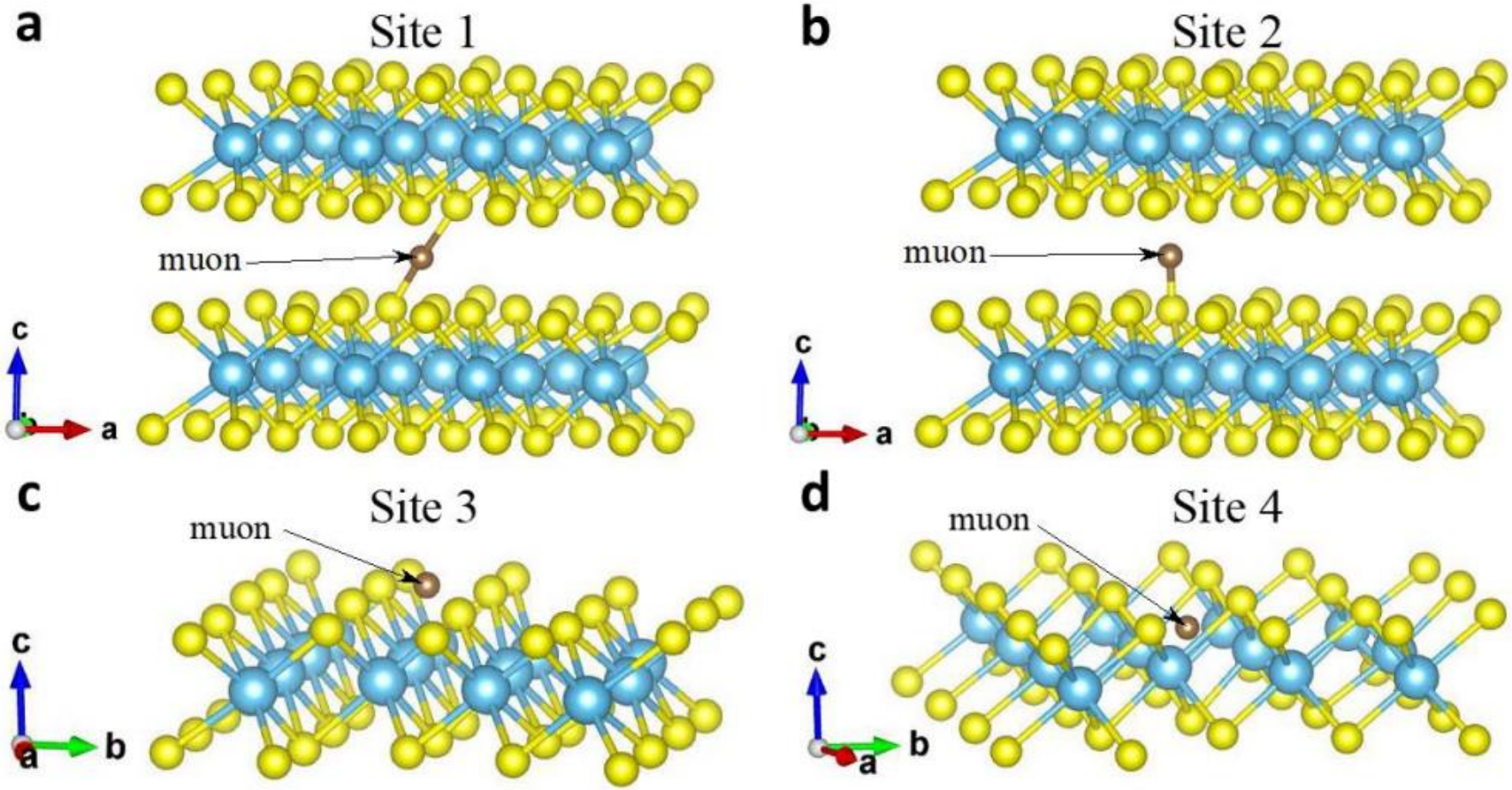
[1]Universidad de Valencia (ICMol), Catedrático José Beltrán Martínez, Paterna, Spain. [2]Centre for Materials Physics, Durham University, Durham, UK. [3]ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, UK. ✉email: francis.pratt@stfc.ac.uk

LF-μSR allows us to study the spin transport



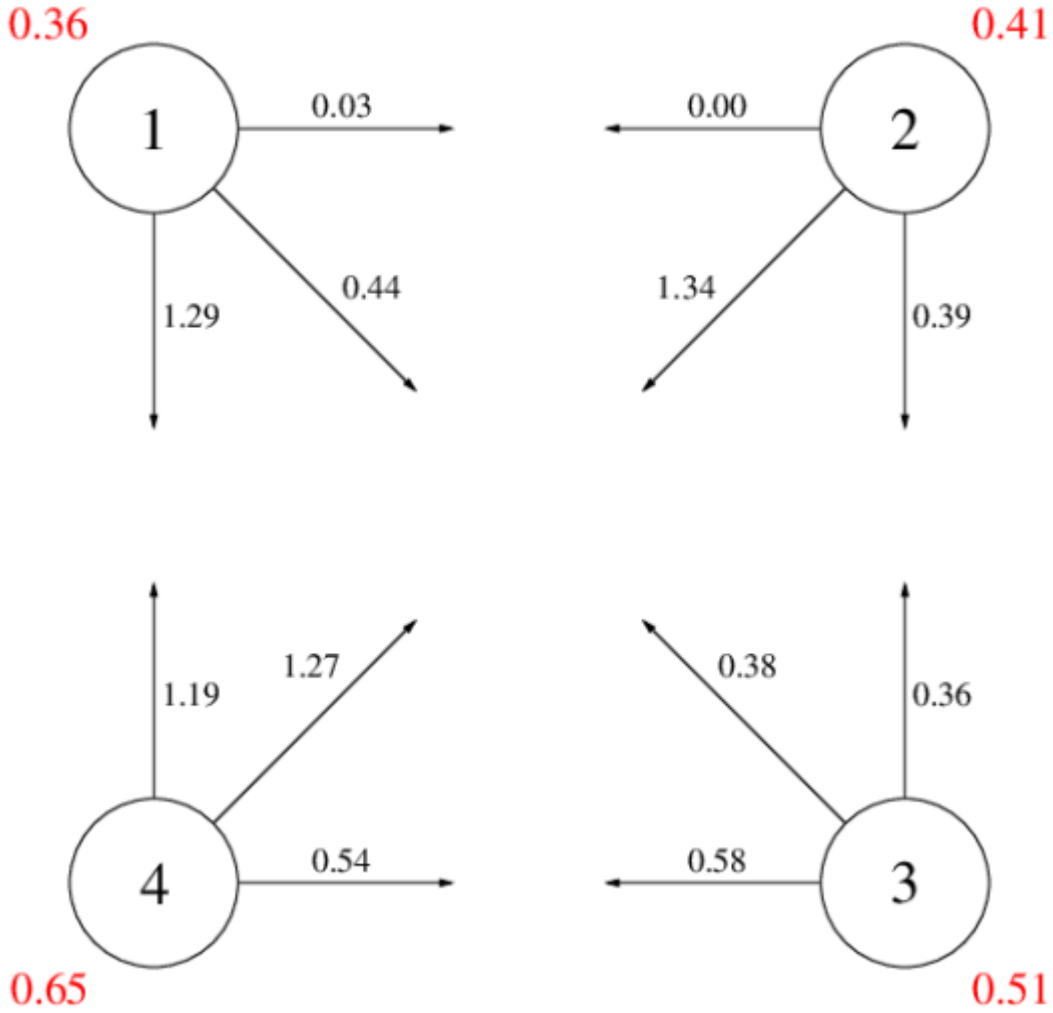


1T-TaS_2 muon sites



Zero-point energies and energy barriers

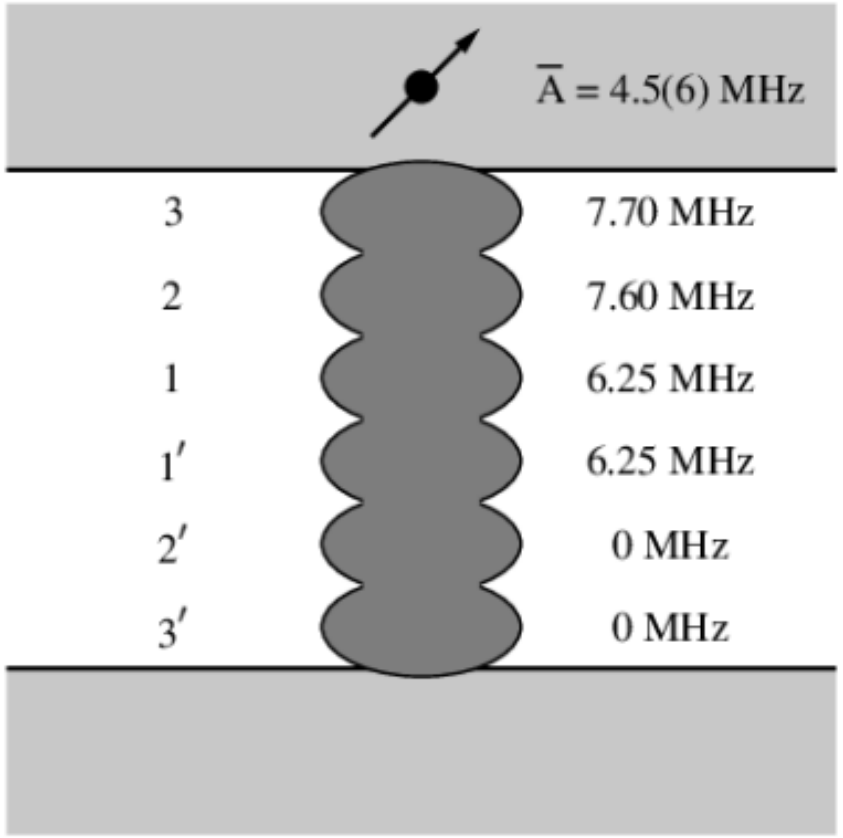
- Zero-point energy (ZPE) can be obtained from phonon calculations
- Energy barriers between distinct sites can be obtained using transition-state search calculations
- Energy barriers between adjacent sites of the same type within *ab* plane all > 1 eV.



Hyperfine coupling

- Coupling of the muon to the spinons is determined by the hyperfine interactions at the muon site

- Due to the delocalisation of the muon, we need to instead consider the average hyperfine coupling to an unpaired spin in a single layer



Example 2 - Muon sites in superconductors with time-reversal symmetry breaking

PHYSICAL REVIEW LETTERS **127,** 237002 (2021)

Intrinsic Nature of Spontaneous Magnetic Fields in Superconductors with Time-Reversal Symmetry Breaking

B. M. Huddart,[1,*] I. J. Onuorah,[2,†] M. M. Isah,[2] P. Bonfà,[2] S. J. Blundell,[3]
S. J. Clark,[1] R. De Renzi,[2] and T. Lancaster[1]
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(Received 28 May 2021; revised 27 August 2021; accepted 27 October 2021; published 1 December 2021)

TRSB in Sr_2RuO_4

Time-reversal symmetry-breaking superconductivity in Sr_2RuO_4

G. M. Luke*, Y. Fudamoto*, K. M. Kojima*, M. I. Larkin*, J. Merrin*, B. Nachumi*, Y. J. Uemura*, Y. Maeno†, Z. Q. Mao†, Y. Mori†, H. Nakamura‡ & M. Sigrist§

* *Department of Physics, Columbia University, New York, New York 10027, USA*
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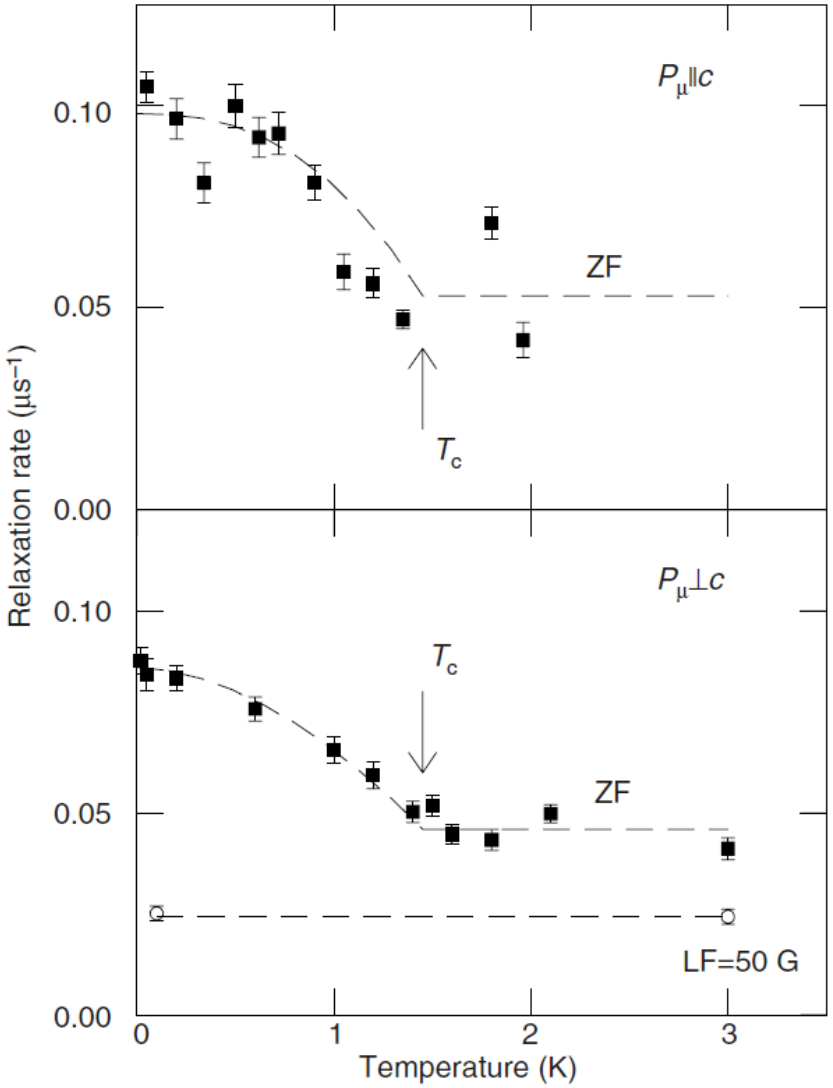
‡ *Department of Material Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

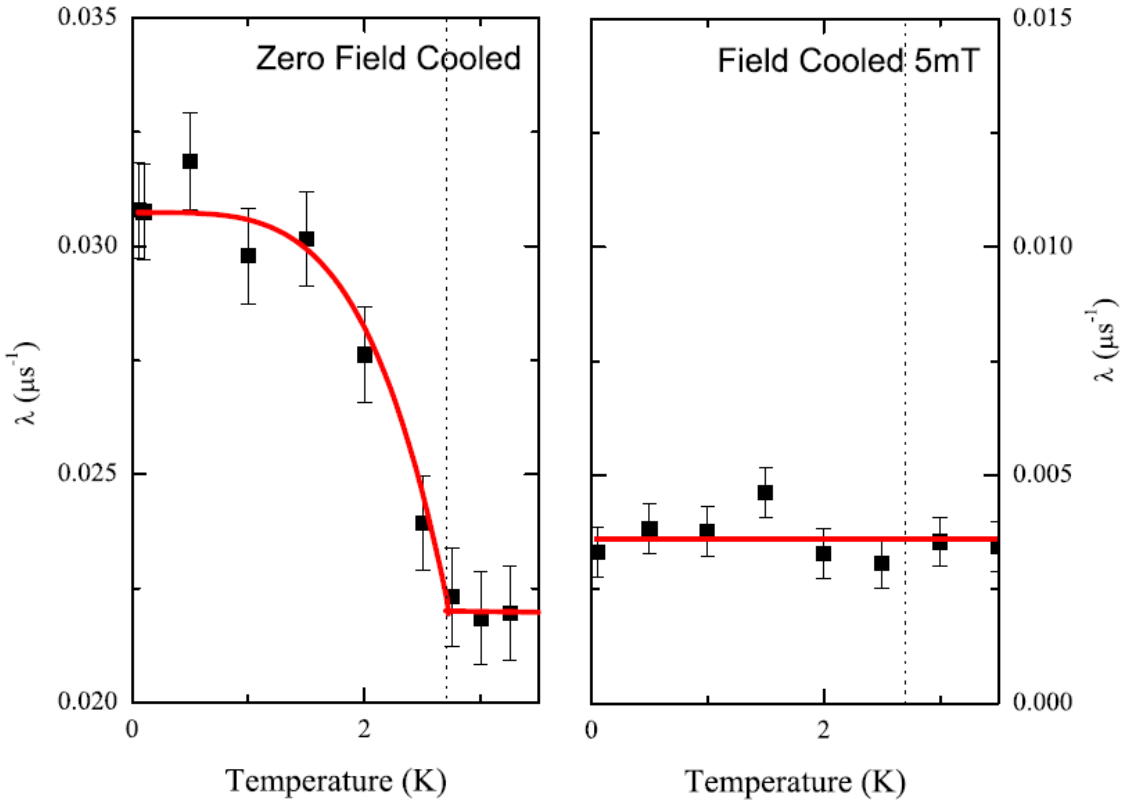
Although the properties of most superconducting materials are well described by the theory[1] of Bardeen, Cooper and Schrieffer (BCS), considerable effort has been devoted to the search for exotic superconducting systems in which BCS theory does not apply. The transition to the superconducting state in conventional BCS superconductors involves the breaking of gauge symmetry

Suggested Cooper pairs with *p*-wave (spin-triplet) symmetry



G. M. Luke *et al.*, Nature (London) 394, 558 (1998)

Noncentrosymmetric superconductor $LaNiC_2$

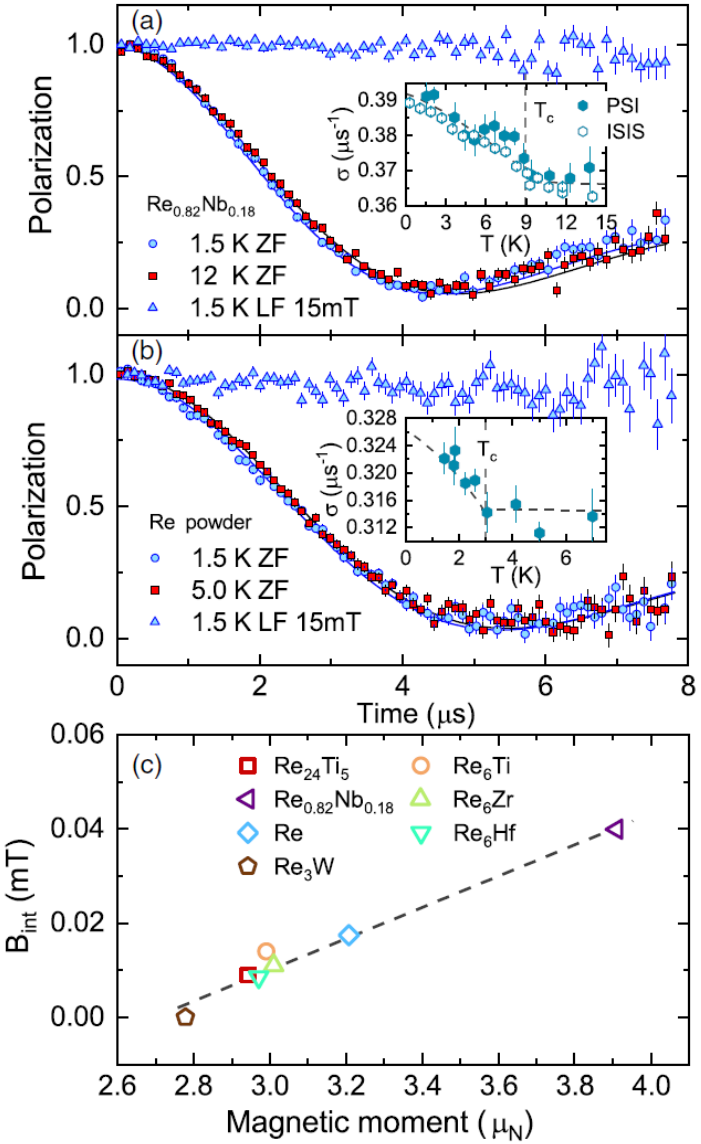


- Analysis suggests four possible nonunitary triplet states compatible with this observation
- Noncentrosymmetric structure allows the breaking of gauge and time-reversal symmetry without breaking additional symmetries of the crystal.

A. D. Hillier *et al.* Phys. Rev. Lett. 102, 117007 (2009)

TRSB in Re-based superconductors

- TSRB observed for (a) $Re_{0.82}Nb_{0.18}$ and (b) elemental rhenium
- Suggests that the local electronic structure of Re could be crucial for understanding TSRB in Re-based superconductors.
- Find that the magnitude of the internal magnetic field scales with the effective magnetic moment



T. Shang *et al.*, Phys. Rev. Lett. 121, 257002 (2018)

Compound	TRSB evidence	B_{int} (mT)	Structure	Space group	Point group	CS?	Gap structure	Proposed state
$U_{1-x}Th_xBe_{13}$	μSR	0.07	Cubic	$Fm\bar{3}c$ (S)	O_h	✓	—	—
UPt_3	μSR, Kerr	0.01	Hexagonal	$P6_3/mmc$ (N)	D_{6h}	✓	Line node	E_{2u} triplet
URu_2Si_2	Kerr		Tetragonal	$I4/mmm$ (S)	D_{4h}	✓	Line + point nodes	Chiral d-wave
UTe_2 [28, 29]	Kerr		Orthorhombic	$Immm$ (S)	D_{2h}	✓	Point nodes	Non-unitary/ chiral triplet
Sr_2RuO_4	μSR, Kerr	0.05	Tetragonal	$I4/mmm$ (S)	D_{4h}	✓	Line node	Chiral singlet
$Ba_{1-x}K_xFe_2As_2$ $(0.7 \lesssim x \lesssim 0.85)$	μSR	0.01	Tetragonal	$I4/mmm$ (S)	D_{4h}	✓		s + is
$Pr(Os_{1-x}Ru_x)_4Sb_{12}$	μSR, Kerr	0.06	Cubic	$Im\bar{3}$ (S)	T_h	✓	Full gap, point node	Multicomponent d-wave
$Pr_{1-y}La_yOs_4Sb_{12}$ $(y < 1)$	μSR	0.06	Cubic	$Im\bar{3}$ (S)	T_h	✓	Full gap, point node	—
$Pr_{1-y}La_yPt_4Ge_{12}$ $(y < 1)$	μSR	0.02	Cubic	$Im\bar{3}$ (S)	T_h	✓	Point node	Non-unitary p-wave
SrPtAs	μSR	0.007	Hexagonal	$P6_3/mmc$ (N)	D_{6h}	✓	Full gap	Chiral d-wave
CaPtAs	μSR	0.08	Tetragonal	$I4_1md$ (N)	C_{4v}	×	Nodal multigap	
$Re_{0.82}Nb_{0.18}$	μSR	0.04	Cubic	$I\bar{4}3m$ (S)	T_d	×	Full gap	LSC
Re_6(Zr,Hf,Ti)	μSR	0.02	Cubic	$I\bar{4}3m$ (S)	T_d	×	Full gap	LSC
Re	μSR	0.02	Hexagonal	$P6_3/mmc$ (N)	D_{6h}	✓	Full gap	—
$LaNiC_2$	μSR, SQUID	0.01	Orthorhombic	$Amm2$ (S)	C_{2v}	×	Two full gaps	INT
$LaNiGa_2$	μSR	0.02	Orthorhombic	$Cmmm$ (S)	D_{2h}	✓	Two full gaps	INT
La_7(Ir,Rh)$_3$	μSR	0.01	Hexagonal	$P6_3mc$ (N)	C_{6v}	×	Full gap	Singlet dominated mixed state
Zr_3Ir [30, 31]	μSR	0.008	Tetragonal	$I\bar{4}2m$ (S)	D_{2d}	×	Full gap	Singlet dominated mixed state
(Lu,Y,Sc)$_5Rh_6Sn_{18}$	μSR	0.06	Tetragonal	$I4_1/acd$ (N)	D_{4h}	✓	Full gap	Multicomponent singlet or triplet

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Importance of the muon in probing TRSB

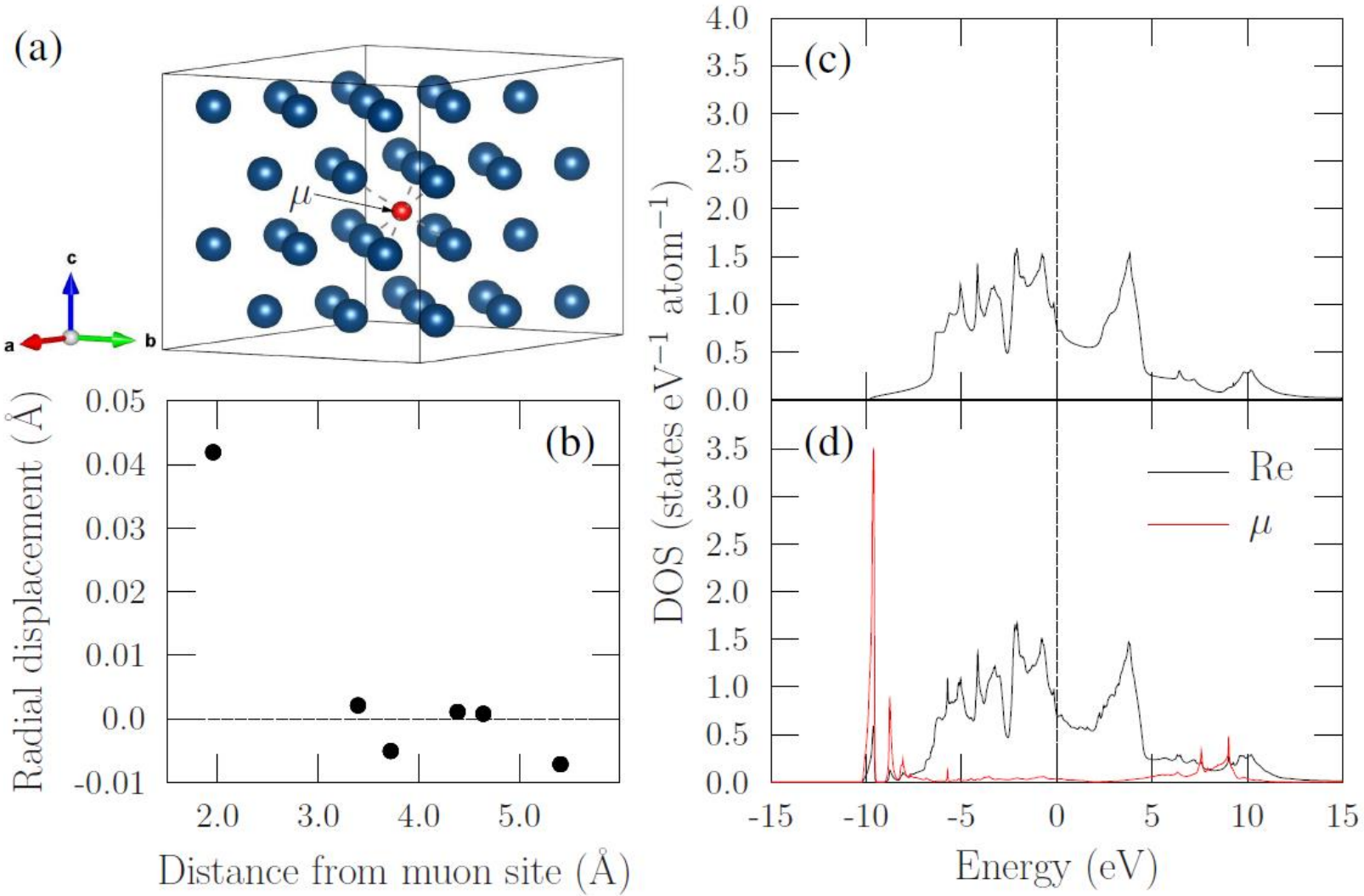
- In most cases evidence of TRSB has only been observed using μSR
- Independent confirmation of the broken TRS is difficult to obtain.
- It is therefore important to understand how the muon interacts with the crystal in these systems, and whether this might have an effect on any magnetic fields it measures.

TRSB Superconductors

Carried out a systematic study of muon stopping states in superconductors that have exhibited spontaneous magnetic field in μSR experiments

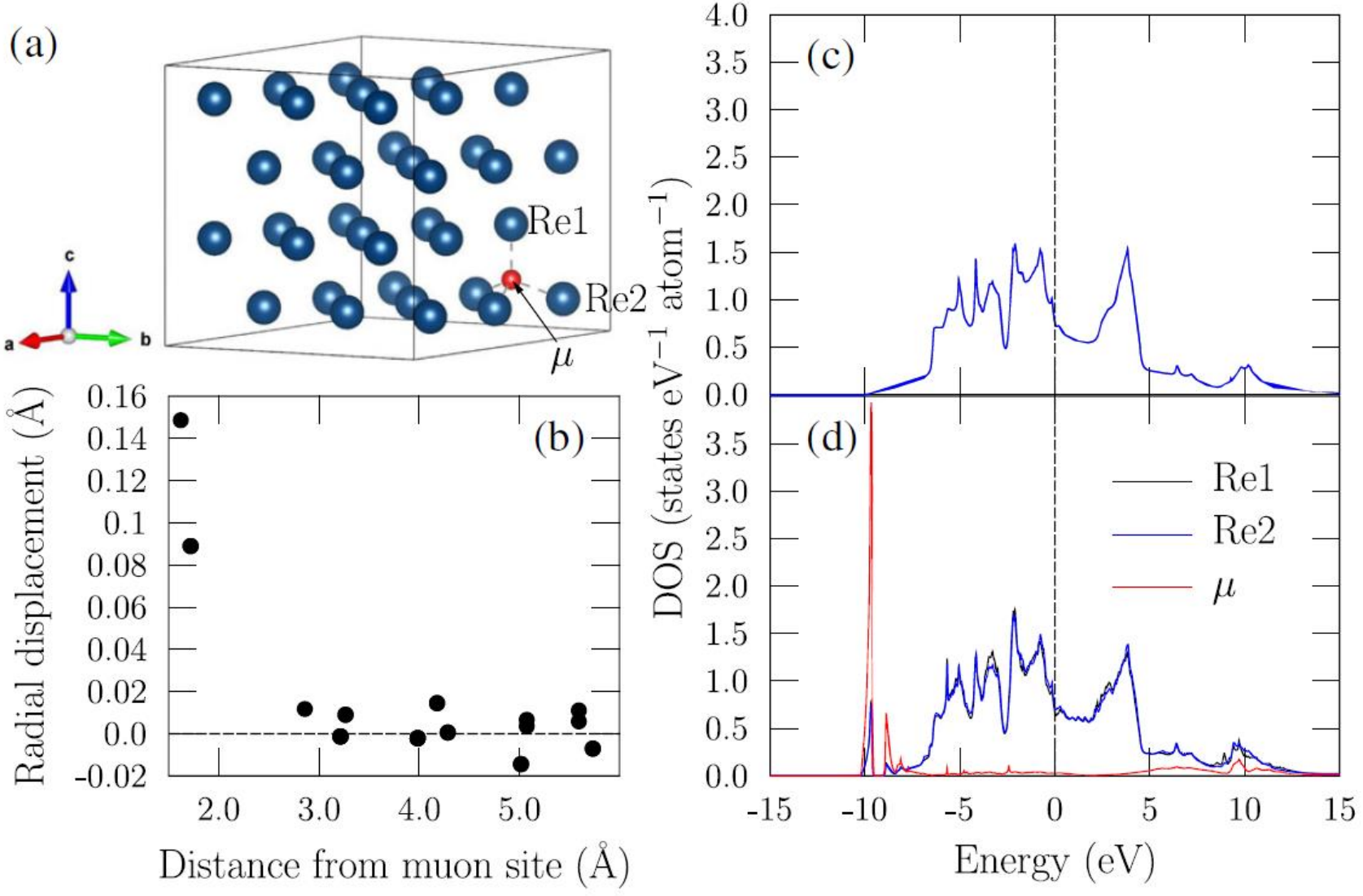
- Sr_2RuO_4
- $LaNiC_2$
- SrPtAs
- Zr_3Ir
- Re
- Re_6Zr

Re – octahedral site



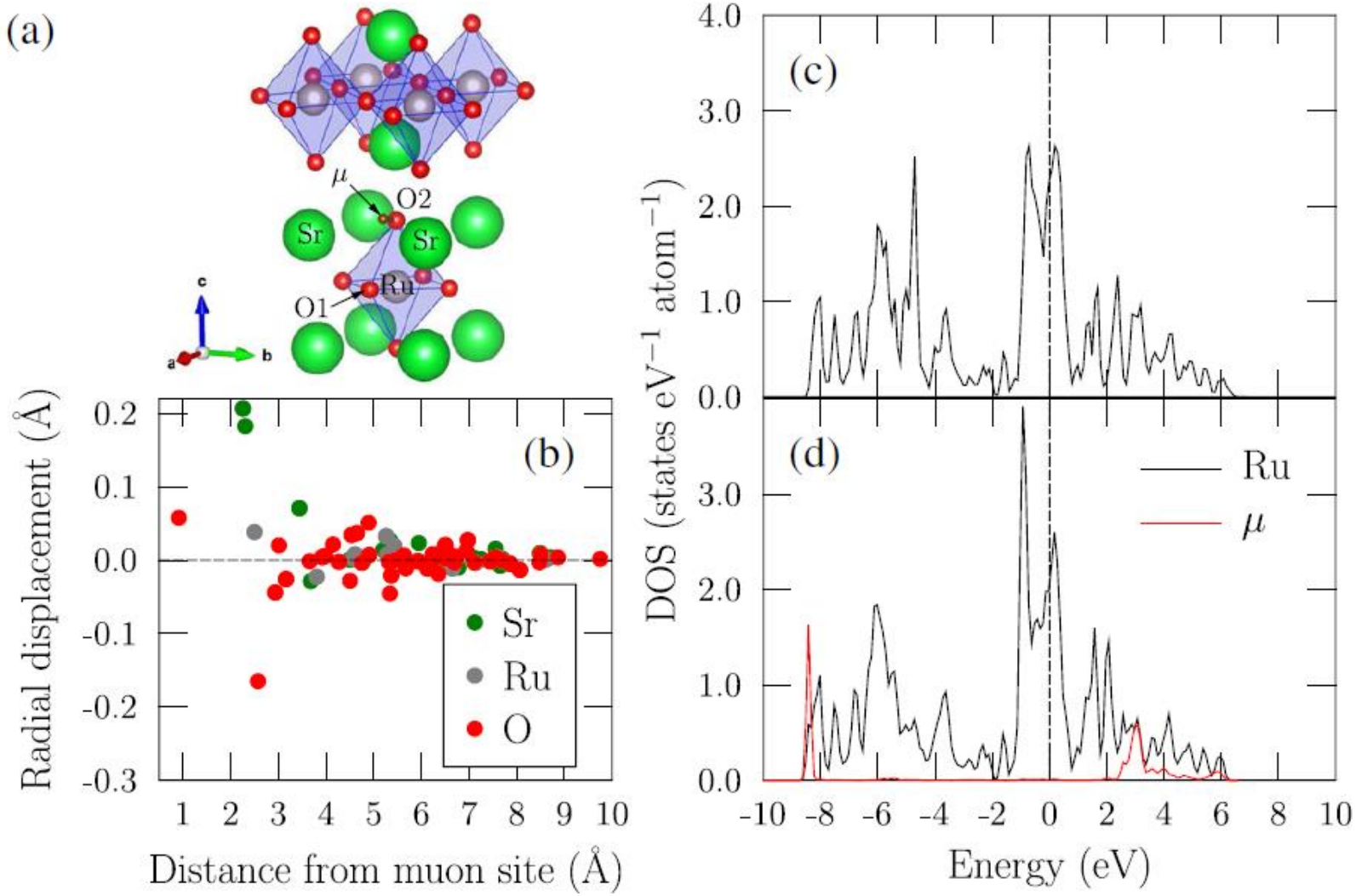
Re – tetrahedral site

0.5 eV higher in energy than octahedral site

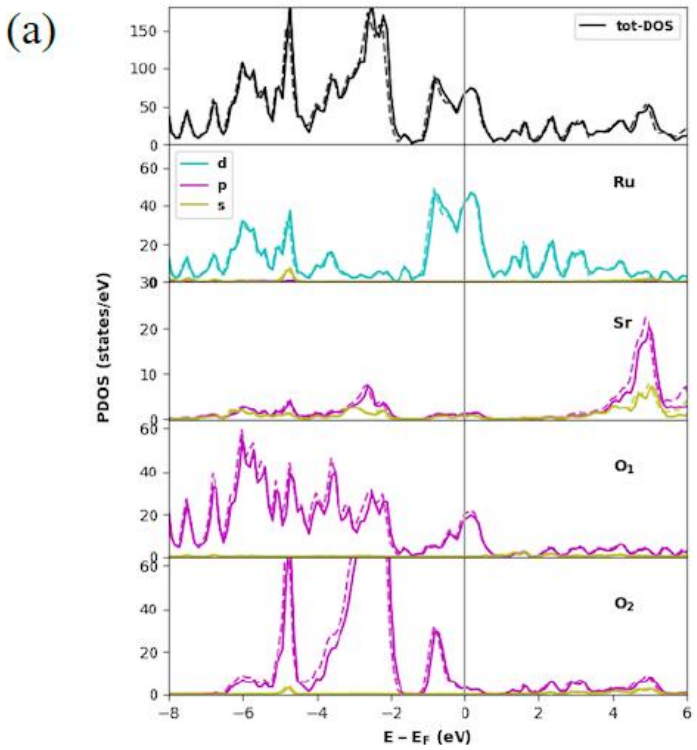


Sr_2RuO_4

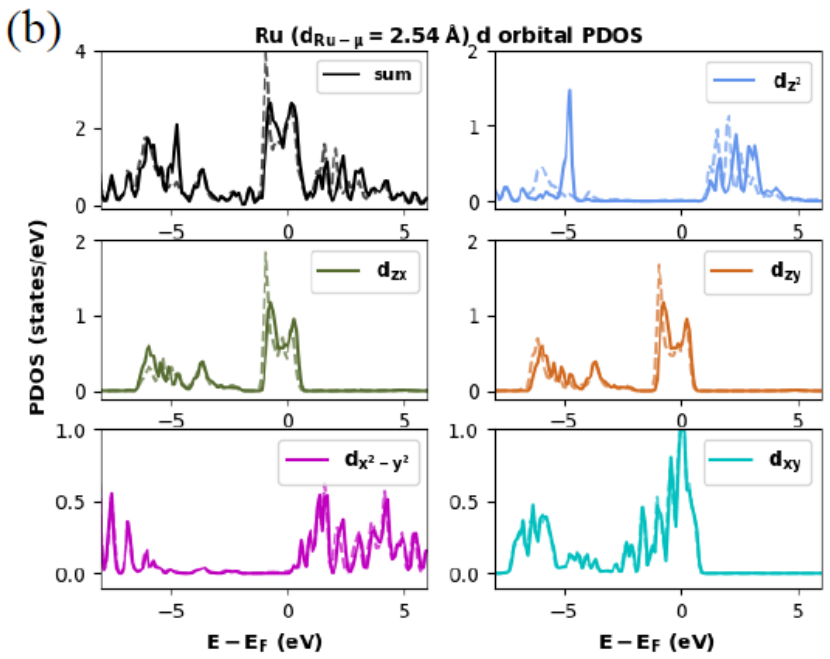
- Muon stops 0.973 Å from an O atom
- Dominant contribution to the DOS near the Fermi energy is that from the Ru atoms



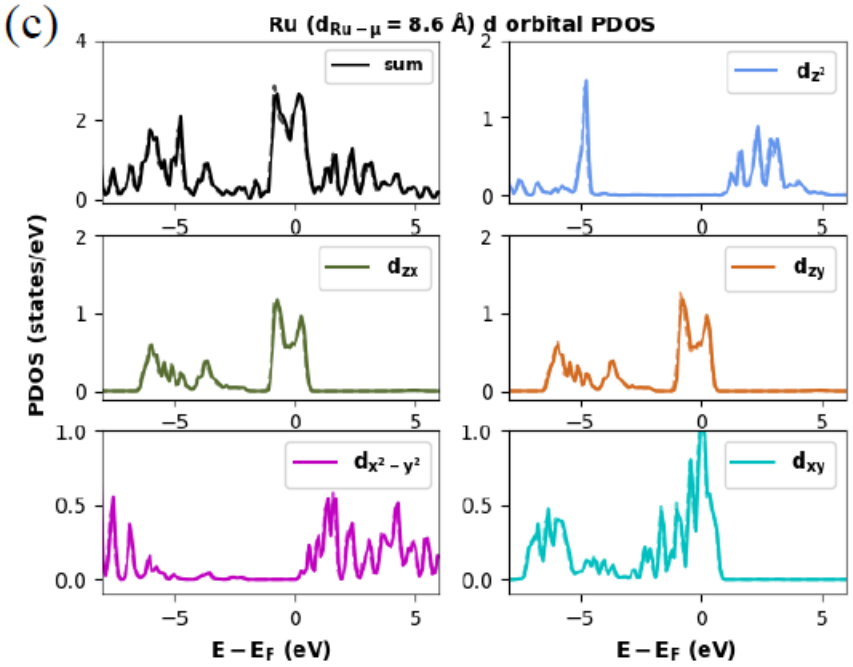
Sr_2RuO_4 – density of states



total



Ru closest to muon



Ru furthest from muon

Structural distortions – summary

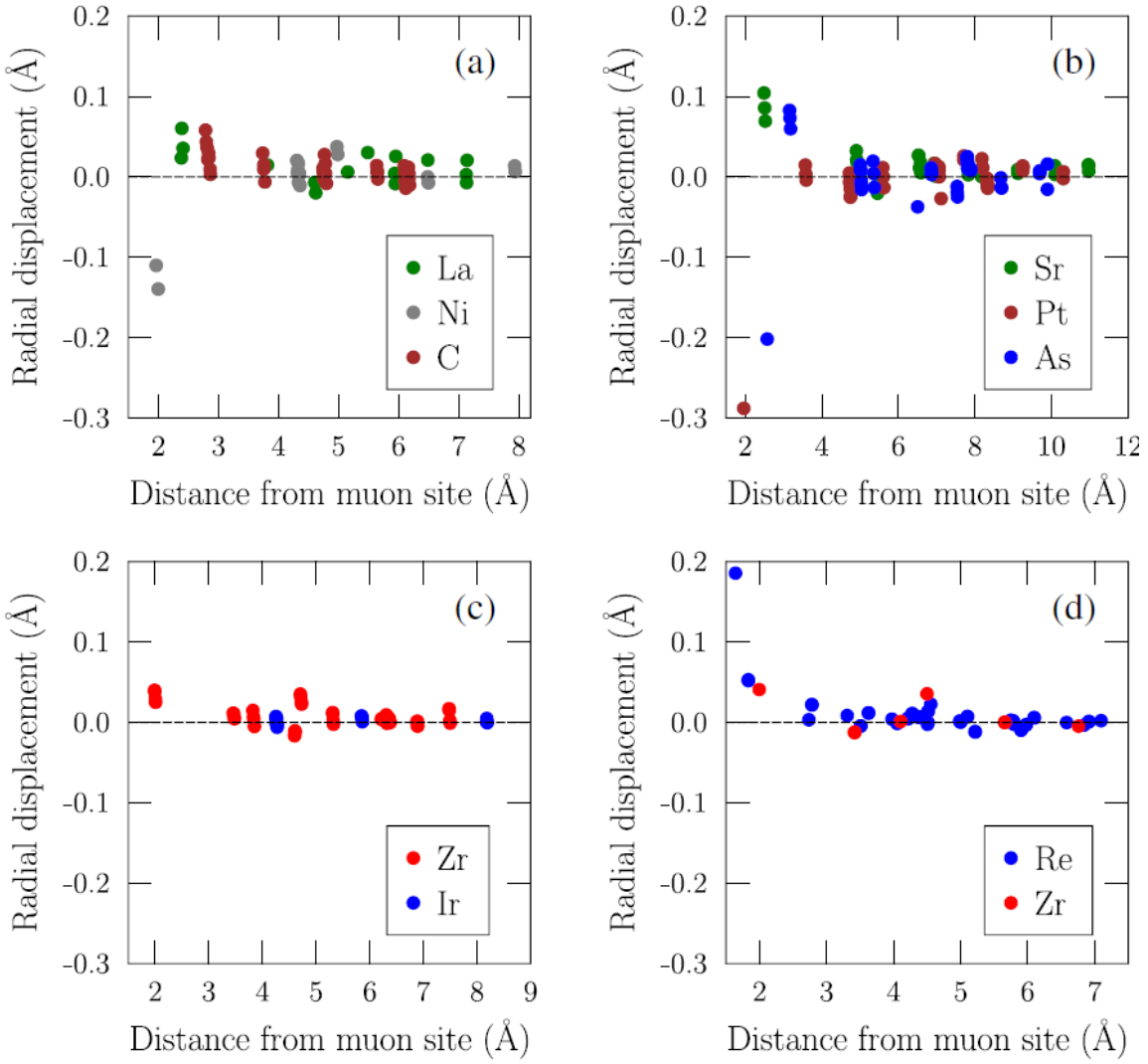
Muon-induced displacements
for lowest-energy muon sites in:

(a) $LaNiC_2$

(b) SrPtAs

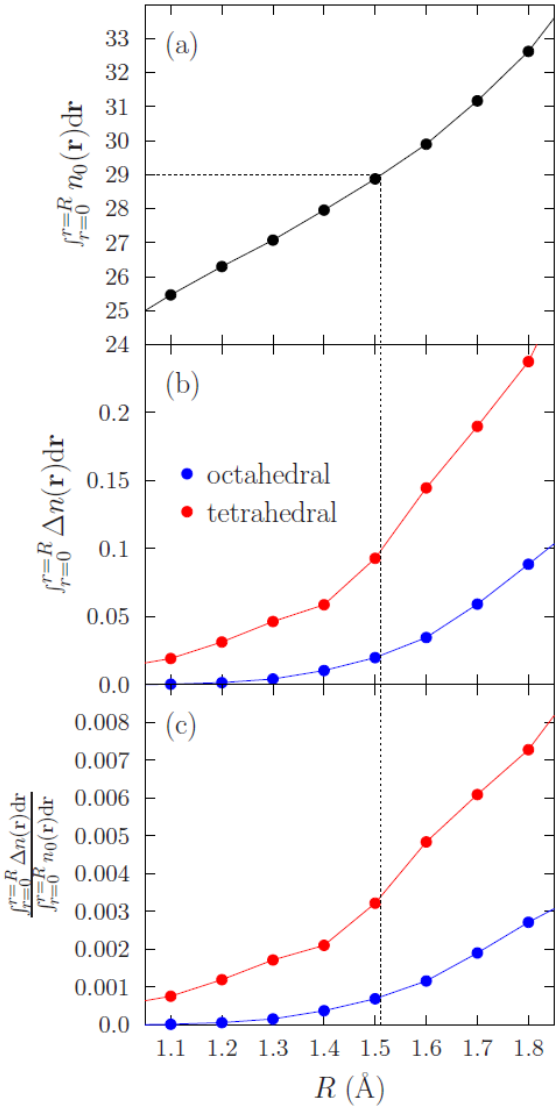
(c) Zr_3Ir

(d) Re_6Zr

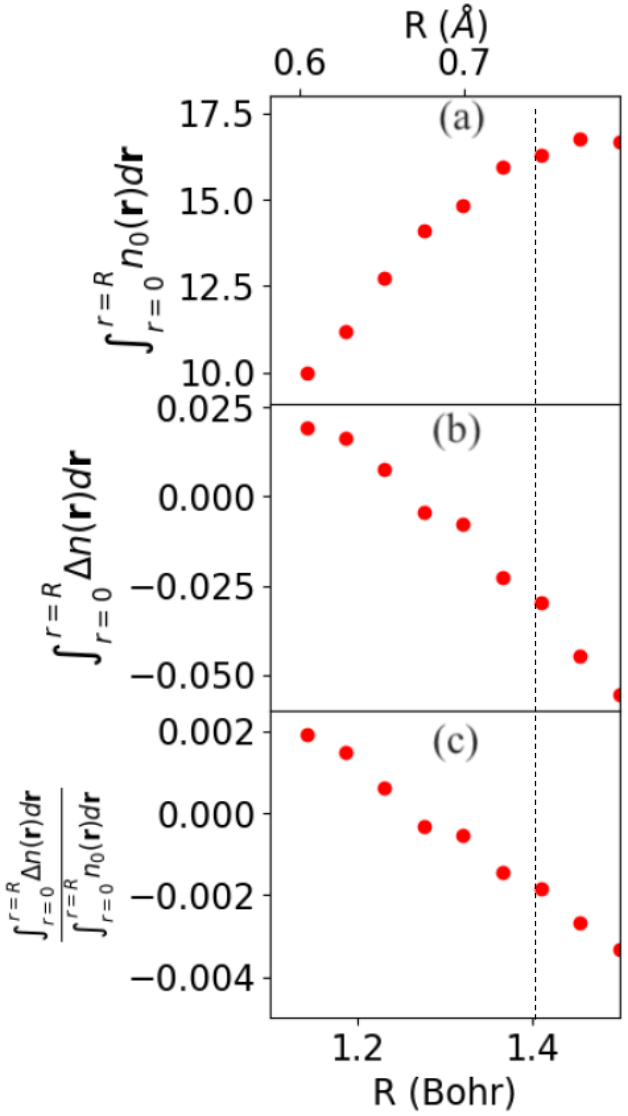


Effect on charge of nearby ions

Re

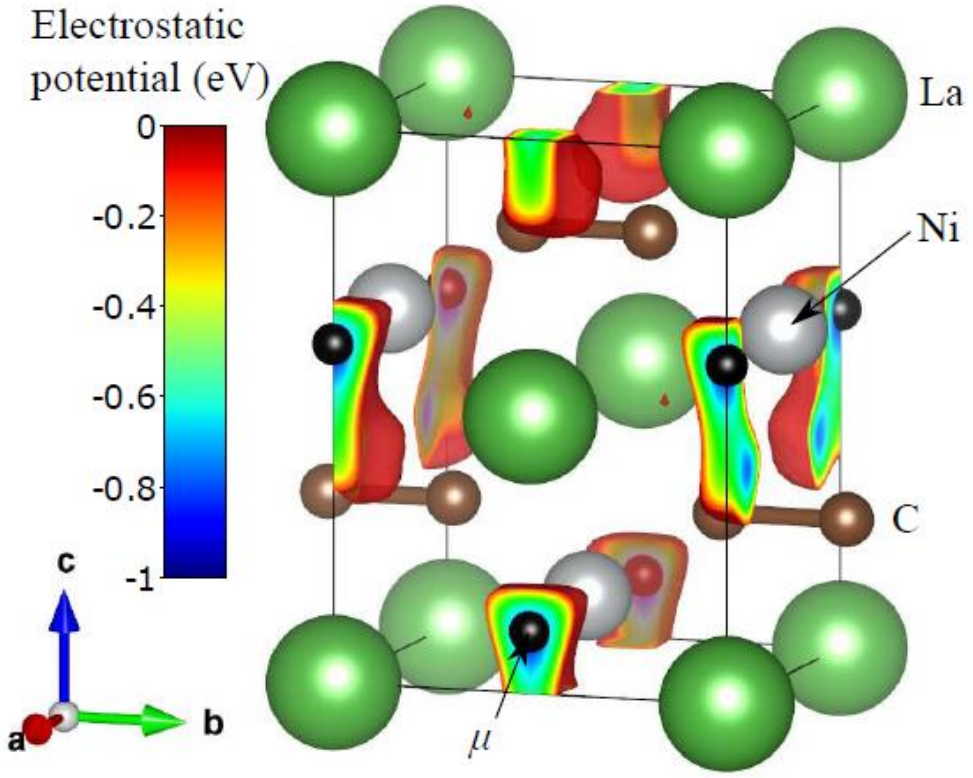


Ru in Sr_2RuO_4



$LaNiC_2$ – effect on spin density

- Spin-polarised DFT calculations
- Muon is triangularly coordinated by three La atoms in the *bc* plane and sits between two Ni atoms along the *a* axis
- Largest changes in spin density occur for Ni, however these are all <0.01$\hbar$/2



Summary

- The muon is not found to have a significant effect on the local arrangement of atoms or ions in its vicinity
- Changes to the electronic structure, including the states associated with the muon occur several eV below the Fermi energy, well away from the superconducting gap (which is a few meV around E_F).
- We therefore conclude that the observation of spontaneous local fields in superconductors exhibiting TRSB is an effect that is intrinsic to these compounds and not a result of a muon-induced effect.

Accessing MuFinder

- MuFinder is available at https://gitlab.com/BenHuddart/mufinder
- Binaries for Windows and Linux are available
- A manual including examples to work through can also be found on this page